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BIOREFINERY, THE FUTURE OF CHEMICAL PROCESS INDUSTRIES

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Abstract

The paper argues that biorefinery is a central issue for the future of Chemical Process Industries with respect to the needs of sustainable development and energetic independence, namely for countries with limited oil & gas reserves, but possessing biomass resources. The latest developments (mid 2015) are briefly reviewed with emphasize on biochemicals, biopolymers and biofuels. The paper presents key chemistry and engineering issues of the valorization routes of biomass. The most interesting bio-building blocks today are methanol for getting olefins, ethanol for replacing fossil ethylene, glycerol, lactic acid, isobutanol, succinic acid, and levulinic acid. Competitive-cost biodegradable polymers are now available, as PLA, PHA, and PHB and FCDA. The market of biofuels is a key trigger of progress in new technologies with benefits for biochemicals too. The technology of lignocellulosic ethanol is reviewed, for which the first commercial plants are on stream. The paper presents also some original research regarding biodiesel manufacturing by solid catalyst.

Key words: biomass, biorefinery, biofuels, bioplastics

1. Introduction

In the context of the finite availability of fossil raw materials, namely of oil and natural gas, the use of *renewable raw materials*, namely of *biomass*, becomes a crucial issue for the future of chemical process industries. The fossil reserves are concentrated in few places, and as consequence they become focal points of geopolitical conflicts. In contrast, the biomass is abundant and more evenly distributed over the planet. For countries having only limited fossil resources, incorporating biomass in the industrial profile can contribute to preserve the energetic independence and bring new opportunities for chemical industry, namely in the field of higher value products. This is the case of Romania, which had in the past a strong oil and petrochemical industry, but is confronted today with the depletion of oil and gas resources. However, the country has favorable conditions for getting cheap biomass, as for example by cultivating energetic crops - as poplar, willow, sorghum and high yield grasses - on lower value land. On this basis Romania could start rebuilding a chemical industry based on the biorefinery concept, more specifically by producing biofuels, higher value chemicals and energy, as it will be later explained in this paper. This approach is fully compatible with the principle of sustainable development, by ensuring economic development based on renewable resources, creating jobs both in industry and agriculture, and protecting the environment.

Figure 1 presents the today's problem of resources. The feedstock for energy and petro-refinery plants are based essentially on the use of *fossil reserves*, namely coal, oil and gas. These industries deliver useful fuels, chemicals and energy for ensuring the fundamental needs of the society, namely for industry and agriculture, food, transportation, heating etc. The output of these activities results in the air pollution by greenhouse gases (GHGs), particle matters (PMs), toxic gases as NO_x and SO_2, as well as in soil and water pollution by waste. Putting in a nutshell, the limited fossil resources are exhausted irreversibly and inexorably, but simultaneously damaging the environment. In 1965 the total world hydrocarbon consumption was about 3.7 billion toe (tons oil equivalent), which rose to 9.3 Btoe/y in 2000 and to 12.7 Btoe/y in 2013. The exhaustion of oil & gas resources is the object of a harsh debate, namely via the model of the "peak" of reserves. Recently, the success of the shale gas in the USA fuelled this controversy. However, it is quite clear that the fossil reserves will exhaust more or less in a short historical time. As very precious, the hydrocarbon resources should be preserved as long as possible. Following the last report of the World Energy Council, in 2011 the ratio world's reserve to production was about 54 years. Note that for Romania this was about 12 years. Taking into account the massive rise of world's population and the legitimate needs for better life, it is obvious that development model based only on fossil resources is not bearable at medium and longer term.

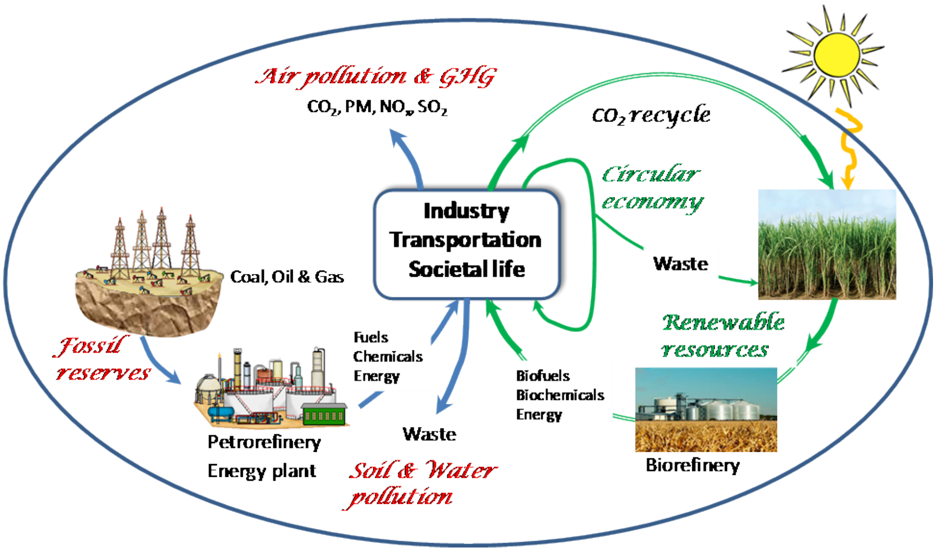

Fig. 1. Fossil resources versus renewable raw materials

Instead, another approach has to be considered, namely based on *renewable resources* and *circular economy*, which means recycling used products and waste. The biomass has the precious property of being the natural energy carrier from the sun to the terrestrial life. Actually, is the biomass at the origin of fossil resources by conversion processes that occurred in the deep ground during several geological periods! Modern chemical technology has to solve the challenging task for replacing fossil hydrocarbon processing by biomass conversion into similar or new products. The technology concept is the *biorefinery*, which supplies, fuels, chemicals and energy for satisfying the needs of the society. The implementation of this model implies the availability of advanced technologies for minimization of energetic and material resources, as well for recycling the waste from agriculture, industry or domestic activities. New green chemistries have to be invented and sustainable process design has to be generalized. These aspects are the topics of this paper.

2. Biomass: availability and composition

Biomass designates materials derived predominantly from plants, which may be used as feedstock in agriculture or industry. From chemical composition viewpoint, biomass is a mixture of complex organic molecules containing for the most part carbon, hydrogen, and oxygen with small amounts of nitrogen and sulphur, as well as traces of other elements, including metals. In the most cases the biomass composition is approximately carbon 47 to 53%, hydrogen 5.9 to 6.1%, and oxygen 41 to 45% (EC sugar platform report, [1]). The presence of a large amount of oxygen makes a significant difference with fossil hydrocarbons. As fuel the biomass is less efficient, but more suited for getting higher value chemicals and bio-products in general.

The biomass used as industrial feedstock can be supplied by agriculture, forestry and aquaculture, as well as resulting from waste materials. The biomass can be classified as follows:

1. Agricultural feedstock

- Sugar crops (sugarcane, sugar-beet, cassava)
- Starch crops (wheat, maize, potatoes)
- Oil crops (rapeseed, soy).

2. Dedicated energy crops

- Short rotation coppice (SRC) (poplar, willow, eucalyptus);
- High-yield perennial grass (miscanthus, switchgrass);
- Non-edible oil plants (jatropha, camelina, sorghum).

3. Lignocellulosic waste material

- forestry wood
- by-products agriculture (straw, corn stover)
- by-products industry (bagasse, paper-pulp)

4. Algal crops from land and see farming

The feedstock origin determines the so-called *biofuel generation*, as presented in Figure 2. The *first generation biofuels* (1G) makes use of agricultural resources, and as consequence they can enter in antagonism with the food chain (edible feedstock). Thus 1G *bioethanol* is produced from starch (corn) and sugar (sugarcane, sugar beet) sources, while 1G *biodiesel* is manufactured as fatty acids methyl esters (FAME) from vegetable oils, namely rapeseed (canola), soya, and palm. However, the merit of the 1G fuels was opening a new chapter in the chemical technology, by setting the bases of large scale biofuels and biochemicals based on renewable raw materials. In particular, the bioethanol manufacturing, now a global leading chemical, brought substantial progress in the fermentation technology, including the development of efficient enzymes and reaction systems. The FAME biodiesel technology evolved from simple batch to more sophisticated solid catalyst processes, with the advantage of supplying large amounts of glycerol, today important feedstock for getting higher value chemicals. Thus, the development of cost efficient technologies for biofuels enables the development of innovative technologies for producing more valuable chemical products.

- Agricultural feedstock:
  - Sugar crops (sugarcane, sugar-beet, cassava);
  - Starch crops (wheat, maize, potatoes, sorghum);
  - Edible oil crops (rapeseed, soya, etc.)
  - Non-edible oil crops (jatropha, camelina);

1 G
biofuels

- Vegetable waste oil (VWO) & waste fats
- Lignocellulosic energy crops
  - Short rotation coppice (SRC): poplar, eucalyptus, willow
  - High-yield perennial grass: myscanthus , switch grass
- Lignocellulosic waste material
  - forestry wood
  - by-products from agriculture (straw, stover)
  - by-products from industry (bagasse, paper-pulp)

2G
biofuels

- Algal crops from land and
  see farming

3 G
biofuels

Fig. 2. Relation between biomass feedstock and generation of fuels

While early biofuels were based on easy extractable sugars and on vegetable oils, the *second generation* (2G) *biofuels* takes advantage from *low-value non-edible biomass*, namely as dedicated energy crops grown on non-arable land, and as waste of lignocellulosic or lipid nature. In addition, there is no connection with the food chain. However, the technology of 2G biofuels is demanding in term of equipment, enzymes and chemicals.

Further progress in sustainability is expected from the *third generation* (3G) *biofuels* based on very high-yield *algal crops*. The algae cultures can be fed directly with concentrated CO_2 streams resulting from industrial processes, as from coal power plants and from fermentation of sugars. The research of industrial farming is in rapid expansion and the results very spectacular. Algae can produce triglycerides similar to those originating from plants, but with a yield higher by an order of magnitude. More recently algal cultures can produce directly various hydrocarbon molecules, including light olefins. The Joule Company (www.joule.unlimited.com) claims the development of CO_2-to-fuel helioculture (cyanobacteria) platforms capable of delivering annually up to 25000 gal/acre (234 m^3/ha) ethanol and 15000 gal/acre (140 m^3/ha) diesel at a price of 1.2 $/gal or 50 $/barrel.

The emergence of 1G biofuels raised strong polemics, mainly because of diverting farmland from the food supply chain and thus increasing the prices, namely in the developing countries (see also the page “food versus fuel” in Wikipedia). It seems agreed today that the effect of biofuels on the food chain should be weak, mainly because of the limitation of surfaces allowed for energy crops, in general at few percentage from the total farmland. In the same time the advent of biofuels incited to substantial improvements in farming technology, both in cultivation and harvesting. Thus after data of American farmers (www.ncga.com), the yield of corn rose with 73% between 1980 and 2015 hitting a record of 173 bu/acres (10844 kg/ha). The yield of conversion to ethanol could rise to 2.8 gallon/bushel (4548 L/ha). This can be still increased by 20% by employing high fermentable starch hybrids. The vegetable cake is employed for feeding livestock, as cattle, pigs and poultry, while the corn stoves may be used for producing energy used in processing, and/or as feedstock for lignocellulosic biorefinery. For a typical yield of 10 to dry biomass/ha, and taking into account an ethanol yield of 400 L/to, it would bring a supplement of 4000 L/ha. Thus, the total ethanol production from corn could reach up to 10000 L/ha. In this way, the manufacture of biofuels can ensure good and stable revenues for farmers. Using only 1.4% of the arable land, Brazil has managed to replace almost 42% of the gasoline with ethanol (www.sugarcane.com)

The cultivation of agriculture crops for biofuels is notable in countries having available large surfaces for agriculture, as USA (corn and wheat), Brazil and India (sugarcane), Malayasia and Indonesia (palm oil), Argentina (soy). It can be noted that *non-edible plants*, as jathropha and camelina, can be grown with good yield for producing biodiesel in developing countries, easing the pressure of importing high-price oil. Europe has only limited farmland surfaces for biofuels, typically cultivated with rapeseed and sugar beet, although some extensions could be envisaged in Eastern Europe.

In the second generation of biofuels, the lignocellulosic feedstock (LCF) consists in energetic crops cultivated on low-value soils or not used in agriculture, by-products from first processing, as bagasse from sugarcane, straw from wheat, corn stoves, as well as municipal or industrial waste. From chemistry viewpoint, a lignocellulosic feedstock contains in general three main useful components: cellulose, hemicellulose and lignin.

Cellulose is the building material of the long fibers of the plant cells. Chemically the cellulose is a polymer of beta-D-glucopyranose $(C_6H_{10}O_5)_n$ of various molecular degree ranging from some hundreds up to several thousand units, depending on the origin of the material (Figure 3). Cellulose can be further broken down by hydrolysis into units of C6 sugars, designated generically as glucose $(C_6H_{12}O_6)$, by employing specific enzymes (cellulase). Note that cellulose is chemically similar with the starch got from maize or wheat, but in which the units are linked by alpha (1-4) glycosidic bonds, which can be broken into glucose units by employing other specific enzymes, as amylase.

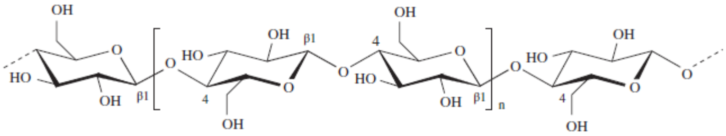

Fig. 3. Structure of cellulosic materials

Hemicellulose is used for building up the short linking fibers of plant cells. It consists of a polymer structure of five types of sugars, mostly based on xylose $(C_5H_{10}O_5)$, but also of C6 glucose of lower molecular degree and random structure, as displayed in Figure 4. Hemicellulose gives by enzymatic hydrolysis mostly C5 sugars.

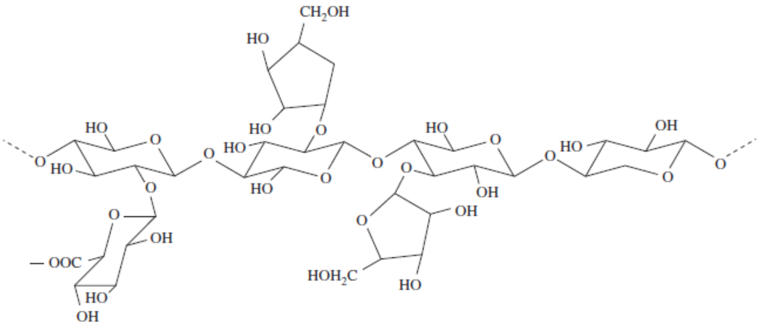

Fig. 4. Structure of hemicelluloses

Lignin contributes to reinforcing the shell of plant cells. Lignin is a complex polymer 3D structure implying phenolic and aromatic acids (Figure 5). Lignin can be used for obtaining more valuable aromatic chemicals from pyrolyse oil, or employed as on-site fuel for generating heat and power. Thus in a LCF refinery the energetic needs of processing can be covered in a large extent by the biomass itself.

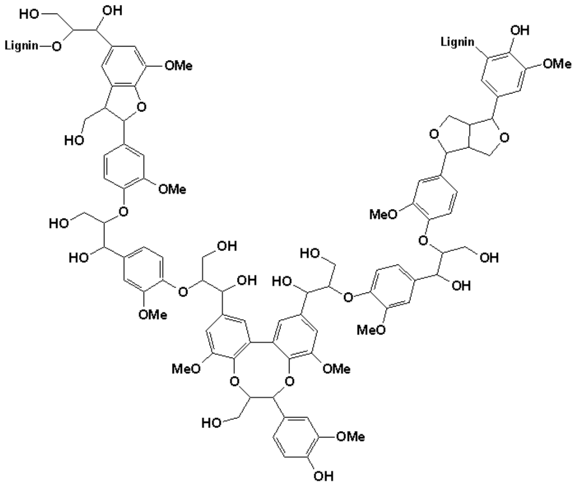

Fig. 5. Structure of lignin

The chemical composition of biomass is treated in detail in specialized references, as Kamm et al. [2], de Jong et al. [3], Sadhukan et al. [4]. As indicated in Table 1, typical values are cellulose 30 to 50%, hemicellulose 10 to 40% and lignin 5 to 30%. Inside the hemicellulose the proportion of C5 and C6 polysaccharides is an important parameter. Inside the same type of biomass there is a large variation of composition depending on plant species, local weather conditions, soil characteristics, harvesting methods etc. Therefore the pre-treatment of biomass becomes a key stage in a lignocellulosic biorefinery.

Table 1

Typical composition of biomass, (wt%)

Biomass	Cellulose	Hemicellulose	Lignin
Softwood	35-40	25-30	27-30
Hardwood	45-50	20-25	20-25
Wheat straw	33-40	20-25	15-20
Corn stoves	35-41	17-28	10-17
Switchgrass	30-50	10-40	5-20

Other composition characteristics of biomass are important for the process design. For example, for the assessment of gasification-type processes the *proximate analysis* is used to determine moisture, volatile matter (VM), fixed carbon (FC), and ash content. The *ultimate (elemental) analysis* gives the chemical composition in terms of carbon, hydrogen, oxygen, nitrogen, sulfur and ash content. This analysis allows determining the high heating value (HHV) of biomass when used as combustible.

3. Biorefinery concept

There is an analogy between petroleum refinery and biorefinery (Figure 6). A classical refinery handles *oil & gas feedstock* for supplying energy *fuels* for transportation and heating, by delivering in the same time a large amount of *energy* (steam, grid electricity). In an integrated *petrochemical complex* the raw materials are converted firstly to *petrochemical building blocks*, primary olefins and aromatics (BTX), from which more valuable intermediates and end-user products are obtained, as polymers, rubbers, solvents etc. A biorefinery has analogue functions, but this time using the *biomass* as feedstock. A biorefinery supplies in the first place fuels, chemicals and energy, but also food products for humans and livestock. In viewing of manufacturing chemicals, the processing consists of generating in early steps specific *biochemical building blocks*, the most being functional molecules much more capable for organic synthesis than the petrochemical building blocks.

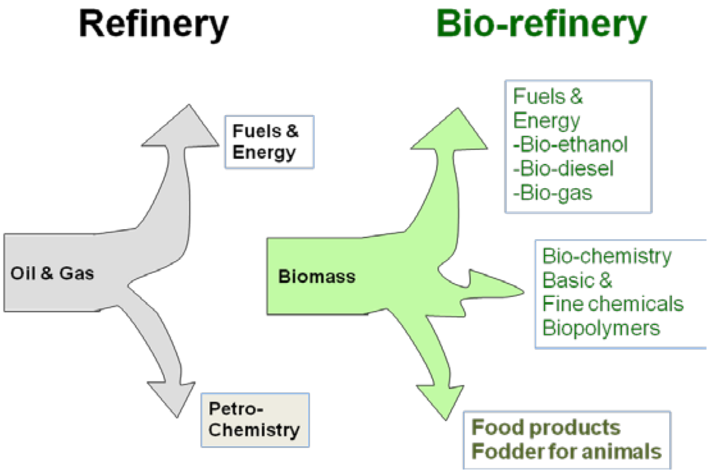

Fig. 6. Analogy between petroleum refinery and biorefinery

Figure 7 presents the essential features of a bio-refinery (Kamm et al. [2], Dimian [5], Denbiras [9]). In the first step, the feed is submitted to *pre-*

processing, from which some *primary products* are directly obtained. An example is *biomass pyrolysis* that leads to *pyrolysis oil* from which some valuable chemicals are got, as alcohols, esters, phenols, and complex organic molecules that otherwise would require complicated organic synthesis. After pre-processing, the conditioned biomass is sent to dedicated *technology platforms*, where it is converted into targeted products.

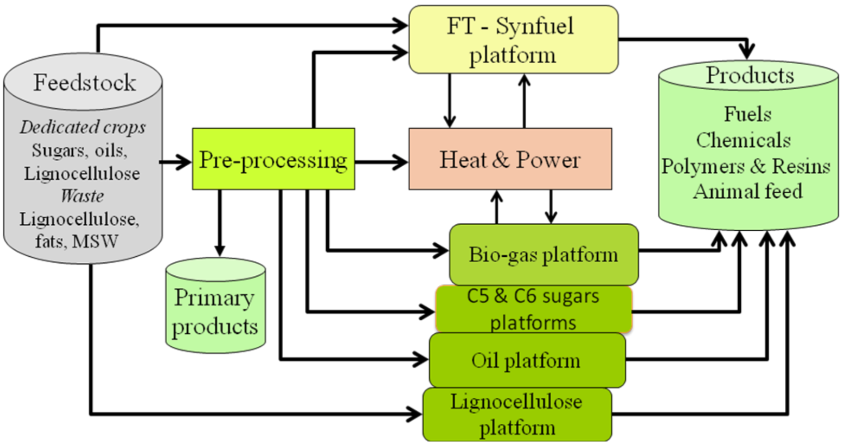

Fig. 7. Biorefinery concept

The platforms are determined primarily by the compositional characteristic of the feedstock and the chemistry routes, as well as by the technology used for conversion (thermo-chemical, biochemical, chemical).

The concept of bio-refinery was the object of an international work of systematization hosted by the International Energy Agency (IEA) as Bioenergy Task 42 (Cherubini et al. [6]; de Jong et al. [7]). Several *technology platforms* have been identified, as follows:

1. Biogas: CH_4 from anaerobic digestion.
2. Syngas: mix CO and H_2 from gasification for Fischer-Tropsh synthesis.
3. Hydrogen by steam reforming, water electrolysis and fermentation.
4. C6 sugars: hydrolysis of sucrose, starch, cellulose and hemicelluloses.
5. C5 sugars: hydrolysis of hemicellulose.
6. Lignin: processing of lignocellulosic biomass.
7. Pyrolysis oil.
8. Oils (triglycerides) from oil crops, algae, and waste oils.
9. Organic juice, as liquid after pressing wet biomass.
10. Electricity and heat, to be used internally or sold to the grid.

The most efficient use of biomass is by an integrated biorefinery complex that consists of coupling the manufacturing of biofuels and biochemicals, analogue to an integrated refinery & petrochemical complex. The goal is getting optimal economic efficiency by the valorization of high-volume low-value (HVLV) bio-fuels with low-volume-high-value (LVHV) bio-chemicals. Some industrial examples of valuable chemical products obtained from bio-resources are listed below:

- biodegradable polymers from PLA (polylactic acid);
- furan dicarboxylic acid (FDCA) polymers replacing polyethylene terephtalate (PET);
- biodegradable polyhydroxibutirate (PHB) polymers replacing polyethylene/ polypropylene;
- propylene glycol from glycerol, and 1,3 propandiol from corn syrop;
- succinic acid by the fermentation of sugars and lignocellulosic waste.

Figure 8 illustrates the concept of a lignocellulosic feedstock (LCF) biorefinery. The feedstock consists of non-edible low value biomass but with high potential for obtaining 2G bioethanol, as well as some higher-value chemicals.

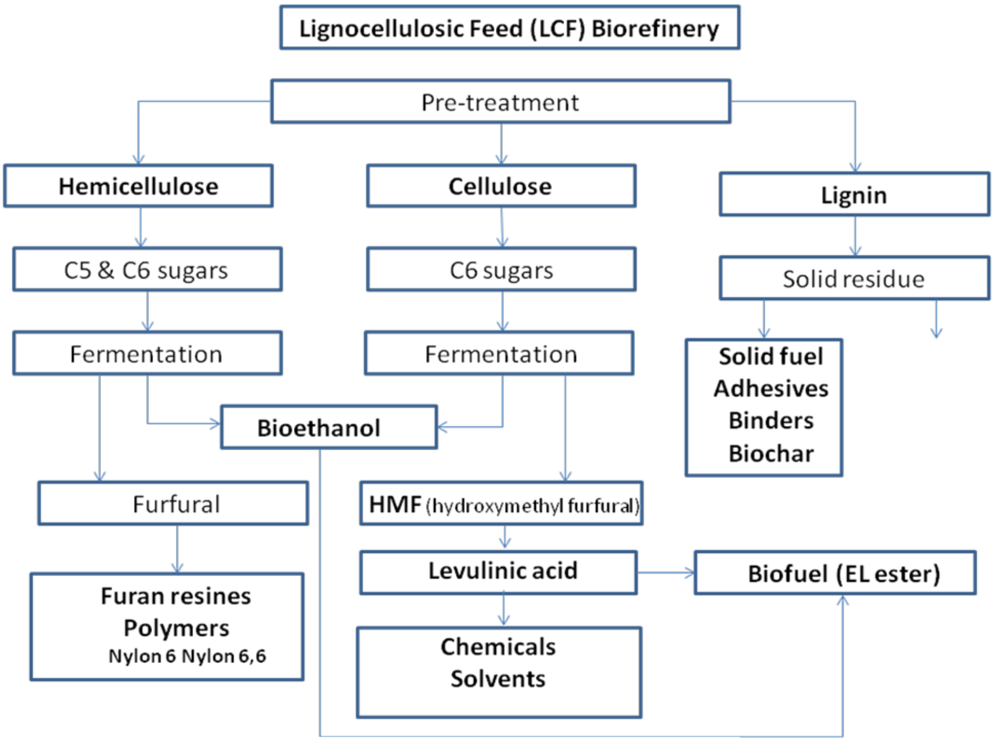

Fig. 8. Lignocellulosic biorefinery platform

The first step is *pre-treatment* in view of separating the main components cellulose, hemicellulose and lignin. Several pre-treatment methods have been developed, as follows (Lin & Luque [8], Amarasekara [29]):

- hydrothermal treatment by steam (biomass explosion) and/or by hot liquid water;

- chemical treatment by ammonia fiber explosion (AFEX), or by acid or alkali hydrolysis;
- biological treatment by specific enzymes;
- treatment by organic solvents and ionic liquids (IL).

These methods have different performances, which depend primarily on the biomass composition, as well as on the target products. Hydrothermal methods are simple and economical. Acid/base boosted hydrolysis is also largely used, but the helping chemicals generate waste streams. The use of solvents may be very efficient, but their recycling is costly. The combination of many factors results in a large number of processing alternatives. In addition, special processing equipment makes the pre-treatment expensive, up to 30% from the total installed equipment cost.

As example, biomass from straw is submitted to steam explosion, and further to hydrolysis with water at higher pressure and temperature. Firstly, the hemicellulose is isolated making free C5 sugars. The remaining matter is submitted to acid hydrolysis or to biological treatment, which gives a cellulose-rich water solution, from which lignin is separated as solid. Sometime a detoxification stage precedes the enzymatic hydrolysis. Next, the sugar solutions are submitted to fermentation by yeast strains. As indicated in Figure 8, typically C6 sugars leads to ethanol and more recently to butanol, as well as to building blocks, as lactic and levulinic acids. C5 sugars may be converted to furfural-based species, and further to a variety of intermediates and plastic materials. Lignin can be used in manufacturing adhesives and binders, or getting aromatics. The global picture gives the message that the lignocellulosic biomass offers large possibilities for manufacturing both biofuels and biochemicals. However, the separation and conversion processes are complex making the technologies difficult and expensive. The specialization on type of feedstock is a way for reducing the costs. Manufacturing bioethanol as 2G biofuel is today the most attractive industrial application of a LCF biorefinery.

4. Chemicals from biomass

The manufacturing of chemicals from biomass starts from *bio-building blocks*, which are simpler molecules on which further diversification is possible by organic synthesis. There is a striking difference between the bio-building blocks and the petrochemical building blocks. In petrochemistry large hydrocarbon molecules present in the feedstock are firstly “chopped” in shorter ones by pyrolysis, and further converted to more reactive functional species by employing energetic intensive methods, as oxidation, hydrogenation, alkylation, chlorination, etc. In contrast, the biotechnology supplies building blocks from biomass by enzymatic processes that need much less energy, since occurring at lower temperatures, typically in the range of 25 to 50 ºC. Besides, the biochemical building blocks are more suited for the synthesis of complex organic molecules, by including already oxygen and nitrogen reactive functions. US Department of Energy published a list of 14 priority chemicals for green chemistry: C3 (glycerol, lactic acid); C4 (L-aspartic, fumaric, succinic, itaconic and malic acids); C4-Oring (furan, butyrolactone); C5 (levulinic and L-glutamic acids, xylitol); C6 (glucaric acid, sorbitol).

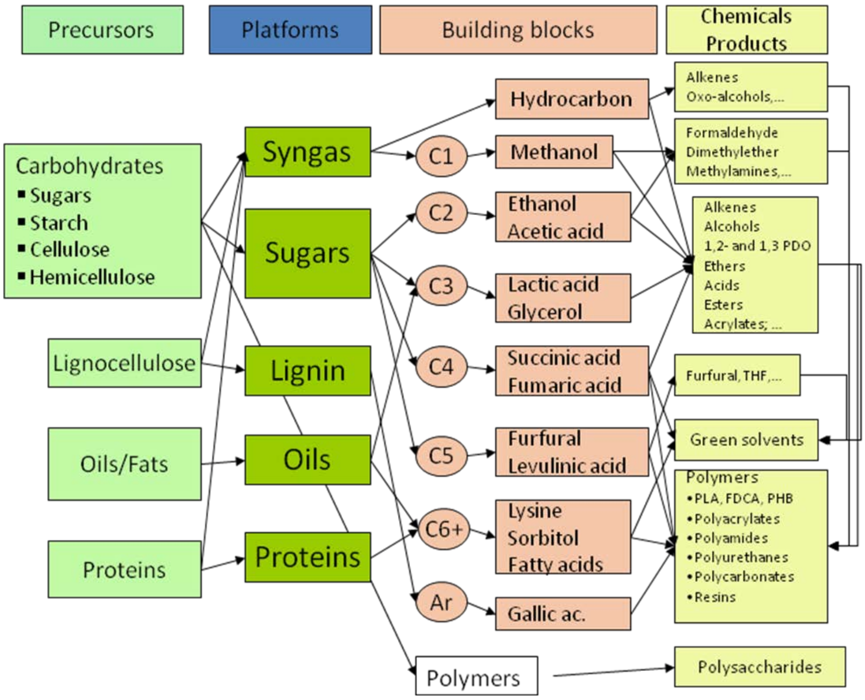

Fig. 9. Building blocks for organic synthesis in biorefineries

Figure 9 presents the main bio-building blocks serving as starting molecules for organic synthesis in biorefineries (Dimian et al. [5, 10]). A comprehensive review regarding the numerous routes for getting chemicals from biomass has been published by Corma et al. [11]. This topic was the subject of several recent works, from which we mention the monographs edited by De Jong & Ommen [3], and Yang, El-Enshasy & Tongchhul [12], as well as the book of Sengupta & Pike [13]. Here we pinpoint only some issues regarding key industrial realisations.

4.1. Chemicals from C1 bio-building blocks

The synthesis of chemicals starting from C1 bio-building blocks can be organized around *syngas* and *methane*, available from waste biomaterials as biogas.

The syngas can be got from biomass by thermal processing, including methane reforming, which may be available in large amounts by the digestion of

Municipal Waste Streams (MWS). Syngas can be converted further in various hydrocarbon species, namely gasoline and diesel fuels, by employing *Fischer-Tropsh technologies*. State of the art of Fischer-Tropsh technologies can be found in the monograph of A. de Clerk [14], as well in the part III of the multi-author book on biomass conversion edited by W. de Jong and J. R. van Ommen [3]. Syngas can recover the carbon practically from every carbonated source, although with low yield. However, getting sustainable hydrogen is challenging; methane remains the best resource.

Methanol is the most valuable C1 chemical. The book of Olah et al. [15] presents an overview of the manufacturing processes, both classical and innovative, as well as numerous applications. Methanol can be got from both fossil (namely coal and methane), and from renewable materials, but also by the hydrogenative conversion of carbon dioxide from industrial exhausts. The conversion of ethanol to gasoline (MTG) is known for about 30 years, but today the most promising is the methanol to olefin (MTO) technology [16]. Several plants have been commissioned so far in China for ethylene and propylene production.

4.2. Chemicals from C2 bio-building blocks

The main C2 bio-building blocks are *ethanol* and *acetic acid*.

Ethanol can be converted easily to *ethylene* and further to a variety of intermediates, as ethylene oxide, ethylene glycol, etc., following the classical routes of the petrochemical ethylene. It is difficult getting competitive ethylene from bioethanol, except when low-cost source is available, as today from Brazilian sugarcane, and in the next years from LCF biorefineries. However, for processes where ethylene is only partially responsible for the raw materials cost, as with vinyl chloride monomer (VCM) and vinyl acetate monomer (VAM), the bio-ethylene can offer a profitable alternative solution, avoiding the need of an oil refinery environment. Note that in the context of a LCF biorefinery there is a twofold cost advantage: 1) the dehydration reaction can be conducted directly with aqueous ethanol resulting from the beer column, saving the energy for dewatering, and 2) the lignin sub-product can contribute substantially for supplying energy by combined heat-and power technology.

Acetic acid can be produced by the fermentation of ethanol. Today the most efficient method is by the carbonylation of methanol. Other valuable chemicals can be further obtained, as esters of acetic acid including vinyl acetate monomer, methyl methacrylate, etc.

4.3. Chemicals from C3 bio-building blocks

The main C3 bio-building blocks are *glycerol*, *propandiols*, *acrylic acid*, *lactic acid* and *acetone*.

Glycerol is available today at low price and in large amounts from biodiesel manufacturing (10% wrt oil feed), but it can be produced also by the enzymatic fermentation of glucose. Glycerol can be employed as drop-in feedstock for traditional petrochemicals, as epichlorhidrine and propylene-oxide. Other synthesis routes emerge from glycerol via acrolein, namely to acrylic acid and methionine, and recently to acrylic acid and acrylonitrile (Dumesic et al. [17]). Two recent innovative technologies can be mentioned: hydrogenation to propylene glycol (EPA Green Chemistry Award, Dasari et al. [18]), and microbial conversion to 1,3 propandiol (1,3 PDO). A process based on corn starch fermentation is commercialised by Dupont for manufacturing Sorona polyester fibres. Technico-economic calculations based on simulation on Aspen Plus^{TM} showed that the production of propandiols is the most profitable (Posada et al. [19]).

Acrylic acid can be obtained from glycerol via acroleine, or by dehydration of 3-hydroxipropionic acid in turn obtained by the fermentation of starch (Ed de Jong et al. [7]).

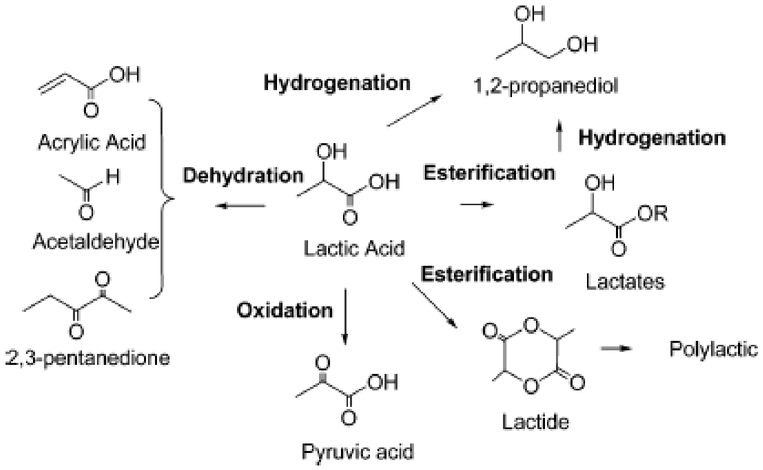

Fig.10. Organic syntheses starting from lactic acid (Corma et al., 2007)

Figure 10 presents routes for chemicals deriving from lactic acid. This can be produced economically by the enzymatic fermentation of glucose. Different chemicals can be obtained, as acrylic acid, 1,2 propandiol, esters, as well as the valuable polylactic acid (PLA).

Acetone can be produced from biomass by fermentation of starch or sugars via the well known acetone–butanol–ethanol (A.B.E) process.

4.4. Chemicals from C4 bio-building blocks

C4 bio-building blocks are based on *butanols, succinic acid* and *hydroxybutiric acid*.

N-butanol produced early by the fermentation of sugars by the acetone-butanol-ethanol (A.B.E) process was not competitive until recently, when technology progress brought this back in the industry, namely in China.

Iso-butanol emerged also newly as a valuable bio-building block for both fuels and chemicals. It can be economically got by the fermentation of both C5 and C6 sugars with special yeasts, as demonstrated by the firm GEVO in USA. Then isobutene can be produced from isobutanol via dehydration. Global Bioenergies in France is developing a process that converts glucose straight to isobutene. These breakthrough developments can open large opportunities, namely as drop-in interrmediates in petrochemistry. Other possibilities emerge through innovative chemical synthesis, as xylene manufacturing. Recently a Dutch consortium has been established to develop a value chain biorefinery around isobutanol in the Rotterdam harbour area [20].

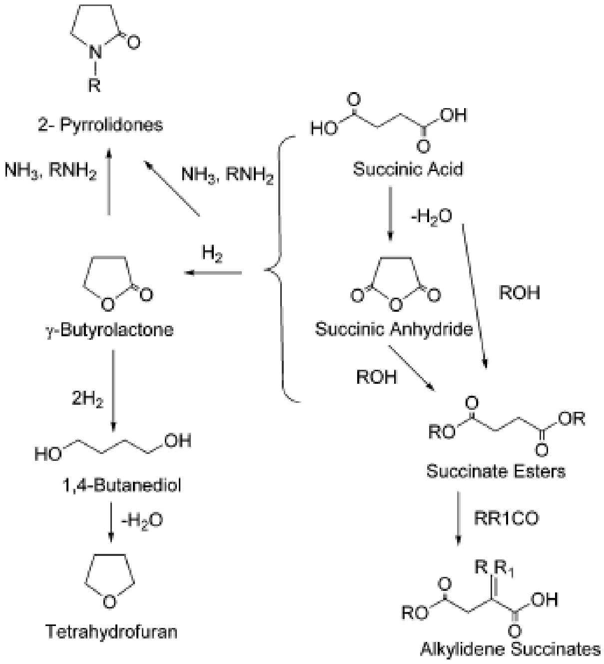

Fig. 11. Organic synthesis starting from succinic acid (Corma et al., 2007)

Succinic acid is a valuable intermediate that can be obtained economically by the bacterial fermentation of sugars. Figure 11 presents important derivatives, as: 1,4 butandiol (BDO), tetrerahydrofuran (THF), pyrrolidone, gama butyrolactone (GBL), and various esters, including polyesters, as polybutylene succinate (PBS).

Hydroxybutiric acid (HBA) is mostly known through its polymer PHBA, which can replace successfully PE based products, but with biodegradability as remarkable added property.

4.5. Chemicals from C4 bio-building blocks

C5 bio-building blocks are *furfural*, *itaconic acid*, *xylitol*, *isoprene*, *glutamic acid* and *levulinic acid*.

Furfural can be obtained from hemicellulose via the fermentation of xylose (C5 sugar). Furfural and its derivatives are important as green solvents.

The manufacture of isoprene and of farnesene from hydrocarbon by the fermentation of sugars is a major advance in bio-technology. T*rans*-β-farnesene is a 15 carbon molecule, 12 long-chain, branched, unsaturated hydrocarbon. It offers unique physical properties and chemical reactivity for new materials. The company Amyris (www.amyris.com) issued from university research is developing industrial processes in cooperation with the fuel company Total.

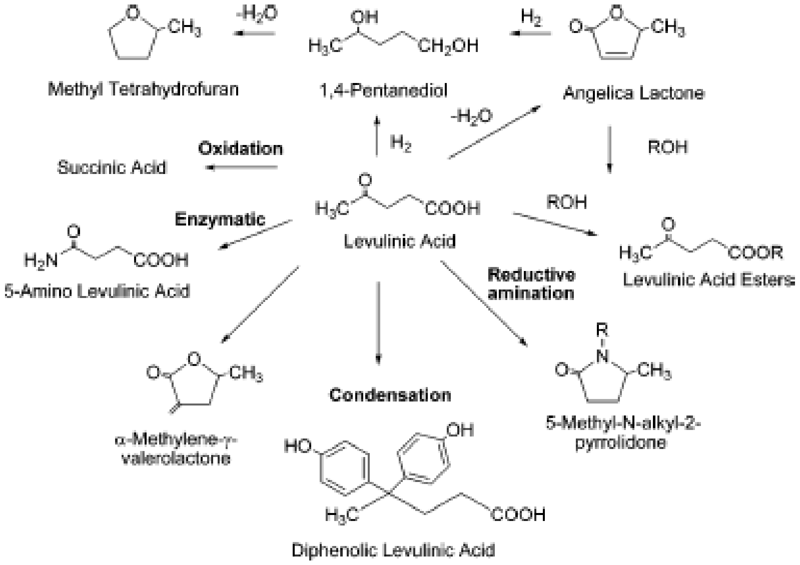

Fig. 12. Organic synthesis starting from levulinic acid (Corma et al., 2007)

The levulinic acid can be produced by fermentation from hemicellulose (C5 sugars), or with better yield from starch (C6 sugars) when an equimolar amount of formaldehyde is also formed. Figure 12 shows the synthesis of a number of valuable speciality chemicals, as lactones and pyrrolidones.

4.6. Chemicals from C6 bio-building blocks

Bio-building blocks in C6 chemistry are *sorbitol*, *adipic acid*, *glucaric acid*, *itaconic acid*, and *2,5-furan dicarboxylic acid* (FDCA).

Sorbitol can be got by the batch hydrogenation of glucose. This method is largely applied in industry. Further derivatives include isosorbide, lactic acid, and branched polysaccharides. Isosorbide is a diol molecule that is obtained by sorbitol dehydration. This can be used in the synthesis of various polymers with new properties, as polyesters, polycarbonates, as well as in the formulation of green plasticizers (Ed de Jong et al. [7]). Leader worldwide in sorbitol is the French company Roquette.

FDCA received recently a particular attention, since it can replace successfully the terephtalic acid in classical PET polymers. Potential synthesis methods are: dehydration of hexose derivatives, oxidation of 2,5-disubstituted furans, catalytic conversions of various furans, biological conversion of hydroxymethyl furfural (HMF). The Dutch company Avantium developed the technology YXY claiming competitive cost for FDCA (Ed de Jong et al. [7]).

4.7. Other chemical products obtained from biomass

Derivatives of fatty acids find numerous applications, namely in polymer manufacturing. A noteworthy example is the production of Rilsan polymer, a 6-11 polyamide made by Arkema-France. This is obtained from castor oil, a triglyceride based on ricinoleic acid, which has the formula 12-hydroxy-9-*cis*-octadecenoic acid, an unsaturated omega-9 fatty acid. As by-products one gets glycerol and heptanal, which can be used in fragrance formulations. Process design issues are in brief presented by Dimian [5].

Other interesting applications find the 36 carbon fatty acid dimmer, diol and diamine. These can be used in the synthesis of various speciality polymers, as polyesters, polycarbonates and polyurethanes (Ed de Jong et al. [7]).

5. Bio-fuels

The production of biofuels is the key direction of development in the use of biomass today. World's biofuels production should reach about 35 billions gallons (133 billions litres) in 2015, from which about 2/3 bioethanol. This figure will probably double until 2021 (Pike Research consulting, www.pikeresearch.com, 2015). About two thirds from the global biofuels are produced today in USA and Brazil, from corn and sugarcane respectively. The efficiency of technology can be measured over the wheel-to-wheel life cycle as total renewable energy produced per unit of fossil energy consumed (RER ratio). In 2009 corn ethanol showed RER values up to 5 by processes employing combined heat and power, while for sugarcane RER was more than 9 with mechanized harvesting (Chum et al. [21]). These cases can be seen as benchmarks for energy crops and perennial high-yield biomass. Note that in both Brazil and USA the surface involved in biofuel manufacturing is less than 2% of the total arable land.

EU set as target at least 10% biofuels in the total fuel mix until 2020. This task is difficult to achieve with 1G biofuels, but it is realistic if 2G technologies are implemented. Therefore, it is useful to have an order of magnitude of the biomass potential in term of biofuels. The theoretical yield may be calculated from the biomass composition. Thus, for ethanol from sucrose by fermentation this is 163 US gallons (617 litres) of ethanol per tonne, but in realistic plant operations it would be about 140 gal (530/l)/tonne. For corn grains the yield is 124 gal (469 l)/dry tonne, for corn stoves and bagasse 112 gal (424)/dry ton, for forest waste 82 gal (310 l)/dry tonne, etc. (Ragauskas, www.ipst.gatech.edu).

As illustration, Table 2 presents typical data regarding the yield of energy crops and the corresponding amount of biofuel produced. It can be seen that energy crops producing 1G fuels offer good yields, namely sugar beet in Europe and sugarcane in Brazil. Corn ethanol is profitable in the conditions of high yield and large scale agriculture in the US Midwest. Sweet sorghum is valuable energy crop suitable for low-value draught land. Rapeseed biodiesel (canola) is mainly used in Europe, while Jatropha in hot climate conditions and low-value land in Africa and Asia. New high yield energy crops emerged in the last years suited for 2G ethanol, as poplar, willow, switch grass and miscanthus. Corn stoves and bagasse are already feedstock for the first commercial lignocellulosic ethanol plants. Very high yields are expected for 3G biofuels from algae, but the biotechnology is only at its beginning.

Second generation bioethanol plants are already on stream and some technical performances are known. The first world's plant opened in 2013 by Beta Renewables in Crescentino-Italy (www.betarenewables.com) has a capacity of 60000 tons/year with feedstock from energy crops and agricultural waste. It handles 270000 tons biomass per year. The investment was of 150 million Euros. The process is energetically neutral and recycles the whole process water (no net water consumption). The first 2G ethanol plant in USA was inaugurated in 2014 by the Spanish company Albengoa in Houghton-Kansas (www.biofuelsdigest.com). It has a capacity of 80000 ton/year with a biomass consumption of 1000 ton/day of agricultural waste collected on an area of 75 km radius. The plant is energetically self-sufficient, but it can even export electricity. In 2015 DuPont announced the opening of a 225 millions $ plant of 100000 ton/year plant in Nevada-Iowa (www.dupont.com). The feedstock is corn stovers collected from about 47500 ha at a rate of 375000 ton/year dry biomass, resulting in a productivity of 3.75 tone biomass/tone ethanol. In this way 600 liters/ha can be added to the ethanol got from corn grains, an increase of productivity of 30%, rising the total yield to over 4 ton ethanol/ha (see Table 2).

Table 2

Typical yield of crops for the first and second generation biofuels

Crops	**RM t/ha**	**Fuel t/t**	**Fuel t/ha**	**Observations**
Sugar and starch energy based crops: 1G ethanol				
Cane sugar[1]	10.4	0.398	4.3	Y=5430 l/ha = 574 gal/acres ; 1 gal=3.785 l ; 1 ha=2.47 acres
Corn grains[2]	9.4	0.348	3.27	150 bu/acre; 2.8 gal-EtOH/bu; 1 bushel=25.38 kg grain
Beet sugar[3]	11.2	0.45	5.04	70 tonne-beet/ha; 160 kg-sugar/ton beet
Sorghum sugar[4]	6-8	0.380	2.3-3.1	3000-4000 l/ha; 2-3 crops/year; Draught resistant
Vegetable oils: 1G biodiesel				
Rapeseed (canola)[5]	3.5	0.35	1.22	40% oil content
Soybean grains[5]	2.9	0.194	0.57	44 bu/acre; 1.5 gal/bu; 1 bu/acre = 0.0673 ton/ha
Palm oil [5]	4.0	0.95	3.8	4 t/ha oil in Indonesia
Cameline seeds[6]	1.9	0.375	0.72	1700 lb/acre; 35 to 38% seed oil content
Jatropha seeds[3]	3.5	0.344	1.2	Resistant to high degree of aridity
Energy crops ethanol: 2G ethanol				
Poplar dry bm[9]	9-16	0.283	2.6-4.6	360 l/dry ton
Switch grass dry[9]	20-40	0.21	4.2-8.4	265 l/dry ton
Miscanthus dry bm[8]	10-30	0.300	3.0-9.0	380 l/dry ton
Lignocellulosic ethanol: 2G ethanol				
Corn stovers	7-15	0.235	1.6-3.5	300 l/dry ton DuPont LCF Iowa plant[10]

1) www.sugarcane.org Brazilian Sugarcane Industry Association May 2015, data 2014
2) www.ncga.com US National Corn Grovers Association accessed May2015, data 2014
3) various web sources
4) www.sweet-project.eu Energy sorghum, an alternative energy crop, 2014
5) www.en/wikipedia.com Biodiesel page accessed May 2015
6) www.cropwatch.unl.edu University of Nebraska, Lincoln, USA
7) www.susoils.com Sustainable Oils Global Clean Energy, Ca-USA, accessed May 2015
8) Cheng, P., Peng, L., Chapter 6 in Biological Conversion of Biomass, RSC EE Series, 2014
9) Ragauskas, A., Biomass to biofuels primer, at GeorgiaTech Univ., www.ipst.gatech.edu
10) www.dupont.com Cellulosic ethanol plant Newada-Iowa, July 2015

5.1 Biodiesel

Two types of biodiesel compatible fuels are today available commercially: fatty acid methyl esters (FAME) and biomass-to-liquid (BTL).

5.1.1 Transesterification of triglycerides with methanol

The material balance shows that when producing fatty acid methyl esters (FAME) biodiesel, one tonne of oil plus 100 kg methanol gives one tonne FAME plus 100 kg of glycerol by-product. The feedstock for biodiesel consists typically of energy crops, as rapeseed in Europe, soya in South-America and palm oil in South-East Asia. Non-edible plant crops can be employed at industrial scale, as camelina or jatropha and in India and in some African countries. Note that the use of ethanol for esterification gives difficult glycerol separation. The transesterification reaction takes place in the presence of base catalyst, homogeneous (K or Na methanoate) or heterogeneous (metal oxides mixtures).

Older processes for biodiesel are of batch type with homogeneous catalysis working at 55 to 60 ºC. The scale-up from laboratory is easy, but the process itself is not very efficient.

Heterogeneous catalyst brings the advantage of continuous water-free process, compact flowsheet and reduced energy, plus getting directly high purity glycerol. This technology was implemented in France at large scale as ESTERFIP process (Bourney at al. [22]). Figure 13 presents a conceptual flowsheet when using heterogeneous catalysis.

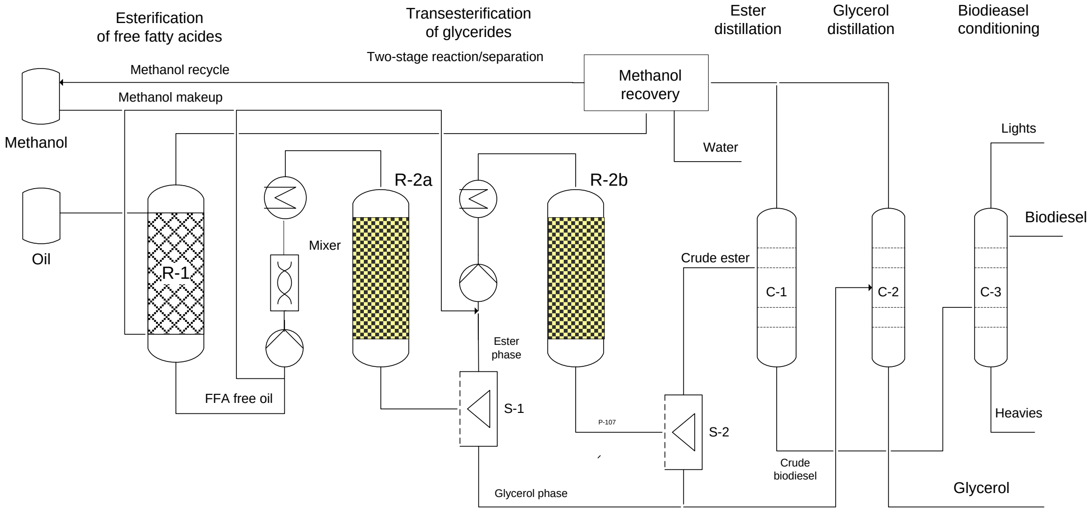

Fig. 13. Process flowsheet for producing biodiesel by heterogeneous catalysis

Raw materials, oil and methanol, enters the first reaction step, for example a reactive distillation set-up (Kiss et al. [23]; Dimian & Rothenberg [24]), which converts free FFA to esters in the presence of superacid solid catalyst. At the top separates a mixture water/methanol sent further to methanol recovery. This step should be considered when treating waste oils, but it is not necessary when handling virgin oils. The bottom stream mixed with methanol and preheated at the reaction temperature, in general around 200 ºC, enters the chemical reactor, which is of adiabatic type. The transesterification reaction is multistep and equilibrium type. In order to progress the conversion over 99%, the reaction needs methanol in excess and intermediate glycerol separation. Two reaction stages are in general sufficient. By heat integration the energetic requirements can be kept low. Note that the ESTERFIP technology makes use of tall tower reactors.

As shown by Dimian et al. [25], when using a solid catalyst there is a relation between the chemical composition of the feedstock, namely the ratio saturated/non-saturated fatty acids and the kinetics of the transesterification reaction, with important consequences on the chemical reactor design. Figure 14 presents kinetic curves time-conversion for three typical raw materials, palm oil, frying fat and soya oil, as well as curves for oleic and linoleic oils.

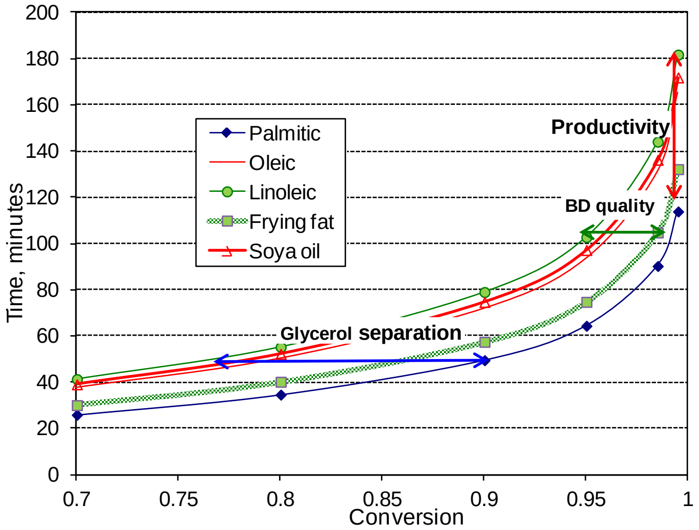

Fig. 14. Relation between the chemical nature of feedstock and the reaction kinetics

The results are valid for talcite-type catalyst, which consists of Mg/Al oxides forming layered-type structures. It can be observed that the kinetic behaviour may be significant different. For example, it takes 120 minute for reaching 99% conversion for frying fat and 180 minute for soya oil. The explanation is that the reaction rate is controlled by the diffusion of bulky glyceride molecules inside the catalyst: saturated fatty acid chains give faster reaction rates, while the unsaturated chains slow down the reaction both by steric and physical bonding effects. In addition, the activity of catalyst can drop in time. The plant operation, as glycerol separation, biodiesel quality (specifications) and productivity, may be severely affected. As consequence, there is need for a reactor design that could ensure variable reaction time and easy catalyst change.

The solution proposed by Dimian, Rothenberg and Schut [26] consists of a plug flow reactor assembled as vertical tubular segments filled with solid catalyst, as shown on Figure 15. In addition, there is a switching valve system (not shown) for connecting and bypassing the reaction tubes, as well for catalyst replacement. The set-up employs static mixers. Heating & cooling elements are provided for mixture conditioning before and after reaction, ensuring in the same time the saving of energy by counter current coupling. Liquid thermal agent (dowtherm, hot oil, etc.) is used for supplying the net hot energy required. The operation conditions for talcite catalyst are temperature of 180 to 230 ºC, pressure 35 to 50 bar, and LHSV of 0.5 to 2 m^3/m^3 catalyst/h. The residence time can be adjusted to the feedstock type and to catalyst activity by varying the number of the active tubes. Moreover, the reaction section can be built by assembling "reaction boxes" designed for achieving a given production rate.

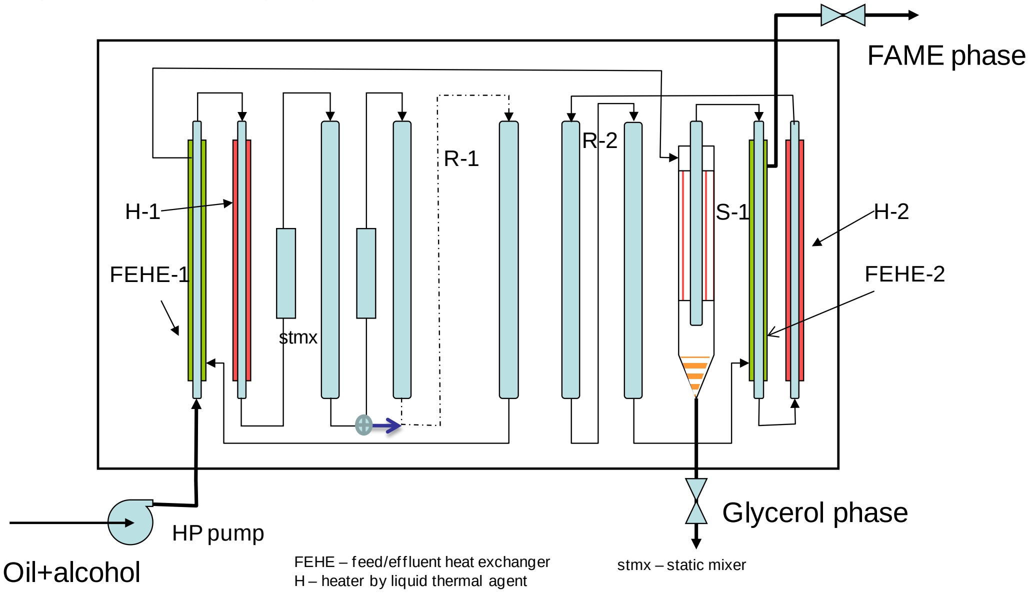

Fig. 15. Compact reaction/separation system using tubular segmented reactor for biodiesel manufacturing European patent EP 2457648 A1 / WO 2012072574 A1 2012

The compact reaction/separation system (Fig. 15) is particularly interesting for *mobile plants*. Taking into account that the hardware is compact and modular (reaction, glycerol separation, methanol recovery, hot oil utility and catalyst maintenance), this can be mounted as containers movable on trucks. The storage tanks (raw materials, finite product), which implies much larger volumes, would remains on the field. This solution is convenient from the viewpoint of seasonal harvesting too. As example, a base module comprising two serpentines each with fifteen tubes of 150 mm diameter and 2.2 m length filled with the tested solid catalyst can yield a biodiesel production of about 7600 liter per day, or 2250 ton per year.

Another innovative solution proposed in the same patent [26] makes use of one-step reaction with recycle after separation by membranes. The kinetic diameter of methanol is 0.38-0.41 nm and the kinetic diameter of glycerol of 0.63 nm. The kinetic diameter of fatty acid alkyl esters depends on the length and unsaturated character of the hydrocarbon chain, and is generally in the range of 0.8 to 1.5 nm. The size of triglyceride molecules is larger by almost an order of magnitude. These size differences allow easy separation of unconverted glycerides molecules from fatty acid alkyl esters, glycerol and methanol. In addition, there are differences in hydrophobic / hydrophilic character of molecules that can be exploited for membrane separation.

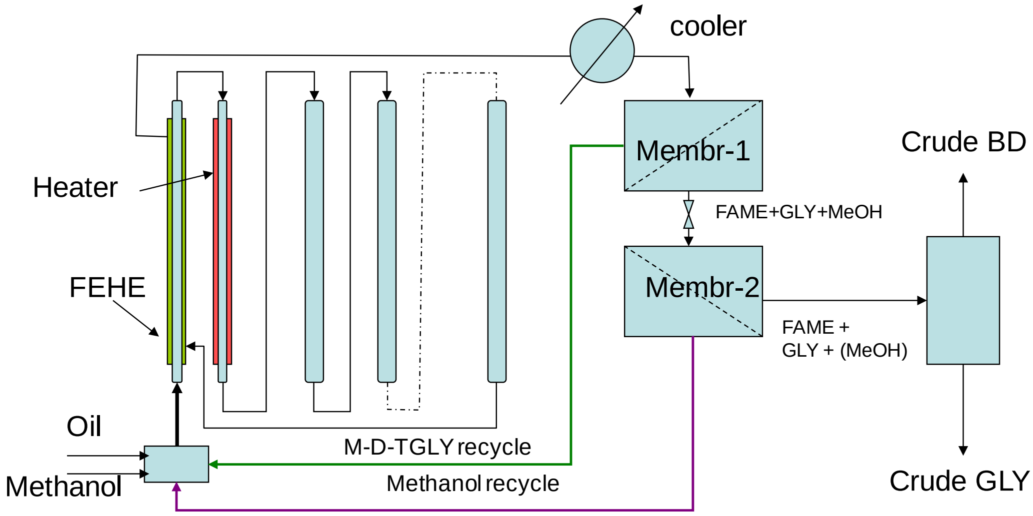

Fig. 16. One stage reaction using tubular segmented reactor and membrane separation for biodiesel manufacturing European patent EP 2457648 A1 / WO 2012072574 A1 2012

5.1.2 Hydrodeoxygenation of lipid feedstock

Another industrial method makes use of the hydrodeoxygenation of lipid feedstock followed by fluid catalytic cracking (FCC). In this way all triglycerides and FFA present in the feedstock are converted to long-chain alkane molecules similar to fossil diesel, delivering propane as by-product. The process was invented by the Finnish company Neste Oy under the licence NesteBTL. By applying the FCC technology the specifications of the final product can be tailored to standard diesel, or to special products, as jet fuel.

Initially the NesteBTL process was developed for using waste vegetable oils and fats, as for example cooking oil and animal fats. For this reason this type of product was called *green diesel*, claiming a 2G type biofuel. However, the processing conditions require a refinery environment, namely cheap hydrogen and FCC plant, being profitable at large capacity, typically over 300 ktons/year. A significant constraint is collecting, storing and transporting large amounts of fat waste. Actually, this method is implemented for dealing with large scale vegetable oil feedstock shipped from overseas plantations to harbour refineries, as palm oil from South-East Asia or South-America sent to refinery sites, as

Rotterdam in Europe or Singapore in Asia. The green label may raise questions. As a conclusion of this section we may add the following comments:

- The FAME technology is still a viable method for producing biodiesel that can be used in mixture with the fossil diesel, producing heating oil or for other purposes. The modern solid catalyst technology can be adapted for small and intermediate scale, offering low investment and low energy consumption. In addition, pure glycerol becomes available at low price, with very positive impact on profitability. FAME biodiesel can put also value on non-edible vegetable oils, as jatropha and camelina, which can grow on low-value soil and harsh climate conditions in developing countries. Building low-cost modular and mobile units is possible by adopting solid catalyst and a smart reactor/separation technology, as shown is this paper.
- The hydrodeoxygenation of biomass-to-liquid (BTL) method allows a unified treatment of both virgin oil and waste feedstock. The technology can be implemented only in an oil refinery environment and at large scale.

More information over technology and design of biodiesel plants can be found in the handbook of Knothe et al. [27], and in the design case studies book of Dimian & Bildea [28].

5.2 Technologies for bioethanol

Manufacturing bioethanol from corn or sugarcane is today well-established. The challenge of the present time is the development of competitive technologies for producing sustainable 2G bioethanol. This is based on lignocellulosic feedstock (LCF). There are numerous pilot and demonstration units, but the first commercial scale plants just emerged in 2013. A list of current projects is available at www.biofuel.org.uk. The first 2G bioethanol plant with a capacity of 75 million litres per year was inaugurated in 2013 in Italy under the label of PROESA^{TM}. The enzymes are produced by the Danish company Novozym. Another important player is the Spanish company ABENGOA, which announced recently a breakthrough in the fermentation technology by the co-fermentation of C5 and C6 sugars. The company started at the end of 2014 a commercial plant of 100 million litres par year 2G bioethanol in Kansas-USA that handles about 350000 tonnes biomass. In addition, the plant may deliver about 18 MW electricity. The Canadian company IOGEN, one of the first players in this field, opened in 2014 in Brazil a 2G ethanol plant with a capacity of 40 million litres per year.

In this section we present some conceptual aspects regarding chemical engineering and process design for lignocellulosic bioethanol. General information can be found in a recent handbook (Amarasekara [29]) and technical reviews [30]-[33]. Figure 17 presents the block diagrams of a plant, adapted from a case study performed by US NREL agency [34]. The first step is the feed handling, which consists mainly from the mechanical treatment of biomass. It follows the pre-treatment phase, discussed previously. Here the biomass is transformed in soluble sugars further submitted to fermentation. The economic success of the technology depends largely of this step; in this case the treatment by steam, ammonia and acid is selected. At this level the outlet biomass stream is diverted to (1) C5 xylose stream derived from hemicellulose submitted to fermentation, and (2) cellulose/lignin stream submitted to enzymatic hydrolysis to supply C6 glucose and further to fermentation. A specialised section deals with the production of enzymes.

The enzymatic hydrolysis and fermentation processes can be accomplished using different strategies: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF) and direct microbial conversion (DMC). A recent review can be found in Telebnia et al. (2010). The fermentation process is slow and takes place at rigorously controlled temperature, pH and substrate concentration. Continuous, batch and mixed arrangements can be used. A modern technique is fed-batch (semi-batch) reactor in which nutritional environment is maintained approximately constant by adding controlled amounts of hydrolyzate and enzymes.

The reactor design is a determinant factor in technology. Compared to petrochemistry, the fermentation reactors are huge, from 10^3 to 10^4 m^3. The mixing pattern of various ingredients at suitable locations for the temperature and concentration control, are more demanding. The availability of appropriate enzymes to handle a specific feedstock is another important issue. At the present time there is no all-purpose enzyme system. The enzymes are rather specialised for handling a typical feedstock, as wheat straws, corn stoves, bagasse, switch grass, etc.

The result of the fermentation is the “beer” solution, which contains ethanol and impurities, as well as solid residues from lignin. After solid separation, sent to burning, the beer is submitted to distillation for getting a near-azeotropic concentrated ethanol. Next, the process deals with the ethanol dehydration. Three methods may be applied: adsorption on molecular sieves, azeotropic distillation with entrainer, and extractive distillation. Finally, the output consists of fuel ethanol, by-products (fusel alcohol), CO_2, and solid residues.

Some data of the NREL exercise are useful as benchmark. Ethanol production 61 US Mgal/yr or 183000 ton/yr. Total installed equipment cost is 232 millions USD, from which the highest costs are the water treatment (50), utility plant (46), fermentation (31), pre-treatment (30), distillation (22), and enzymes production (18). The specific equipment cost is 1270 USD/ton. Total investment cost (TCI) is 422 millions USD at 45% indirect (working) capital costs. The ethanol yield is 79 gal/ton or 400 litres/ton dry biomass. The actual ethanol yield is 76% compared with the stoichiometric yield resulted from biomass composition. The minimum selling price is 2.15 \$/gal at 2007 prices, from which the raw materials are 0.74 \$, auxiliary chemicals 0.31 \$, enzymes 0.20 \$, capital depreciation 0.20 \$, and average return on investment 0.57 \$. Electricity consumption is about 1 kWh/litre and water requirement of 5.4 litre/litre. High costs of chemicals and energy indicate that major progress has to be done in pretreatment and fermentation processes.

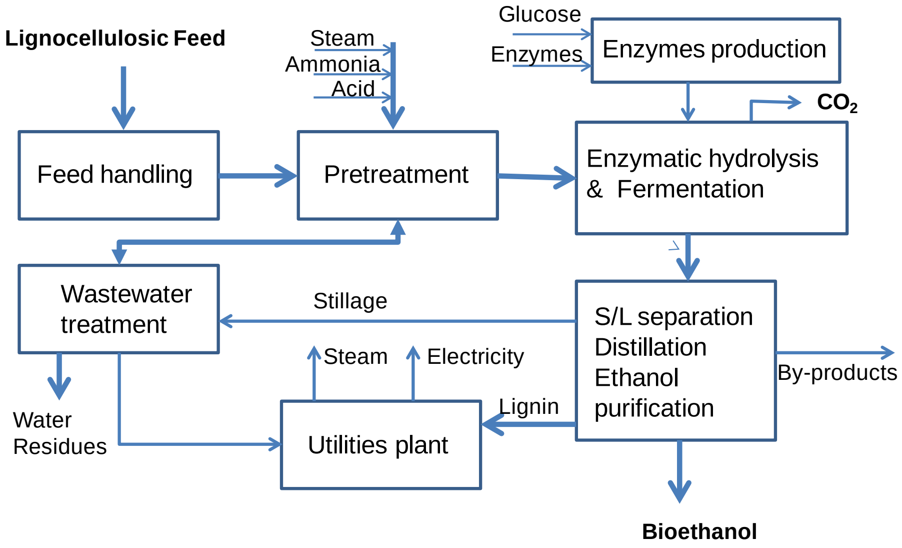

Fig. 17. Block diagram of a lignocellulosic bioethanol plant

5.3 Other biofuels

Bio-butanol can be used as fuel, similarly with ethanol. The advantages are more energy density (about 20% higher than ethanol), reduce oxygen content (lower NOx), and volatility close to gasoline (better ignition). The feedstock is similar to ethanol, including starch and lignocellulosic materials, but the fermentation process makes use of different yeasts. Ethanol plants can be easily retrofitted to butanol plants. It is expected that butanol fuel will know a rapid growth in the next years.

Dimethyl ether (DME) is an alternative fuel with good potential, as substitute for LPG and in mixtures with both gasoline and diesel. The combustion gives very low emissions as CO, NOx and PM. Since available from waste materials DME is considered as a 2G fuel.

6. Bioplastics

Bioplastics are materials that are made totally or partially from renewable raw materials, and in large extent biodegradable/compostable and recyclable.

The manufacturing of high value bioplastics is a central issue of a chemical industry based on biomass. The world's production of biopolymers should be about 2000 kt/y in 2015 and rise up to 6000 kt/y in 2018. The today share is 75% Asia, 12% South-America, 5 % North-America, 8% Europe, from which 62.5% bio-based non- biodegradable and 37.5% biodegradable materials (www.eu.europa-bioplastics.org).

Three categories of bioplastics can be identified:

- Drop-in plastics, identical with petrochemical counterparts, since starting from the same monomer. Examples: bio-PE (ethylene from bioethanol), bio-PP (propylene from biomass).
- Fully bio-based, as polylactic acid (PLA), polyhydroxyalkanoates (PHA), poly-FDCA, thermostatic starch, cellulose fibres, etc.
- Partially bio-based, in which a substantial amount (+ 30%) comes from bio-sources. Examples: bio-PET in which the glycol monomer has a biomass origin, some polyamides, bio-VCM with ethylene from ethanol, bio-VAM, with ethylene or/and acetic acid from biomass. .

The development of the drop-in bioplastics depends in a decisive extent on the profitability of the bio-monomer. For bio-ethylene this condition is fulfilled today only with ethanol from sugarcane in Brazil, but should be meet with the 2G ethanol in the next future. The use of ethylene from biomass should be also profitable in situations where the availability from a refinery complex is neither economical nor possible, but the other co-raw materials should have low price, as mentioned above.

Fully bio-polymers, as PLA and PHA will have a fast development in the next years, since the ecological advantages can overpass the argument of price only.

7. Economic challenges

The market of biofuels, biochemicals and biopolymers is in full expansion. There are good reasons to believe that the growth will accelerate in the next decades, since the use of renewable materials is pushed strongly by the needs of sustainable development. The main effort in research and development in chemical process industries will be oriented in this direction.

At the end of 2013 the size of the market of fossil chemicals was about 330 million tonnes, while the market of biochemicals and biomaterials was about 50 million tonnes. As discussed before, the market of chemicals are only fractions from the market of fuels, as about 10% in USA and Europe. Consequently, the key role in the progress of biorefineries today is played by the biofuels sector, namely with respect to second generation biofuels and the biotechnology of algae.

Table 3

Market for bio-based chemicals and total product markets (after EC report [1])

Product	Bio-based market				Total market (bio+fossil)		
	Price ($/t)	Volume (ktpa)	Sales (m$/y)	% of total market	Price ($/t)	Volume (ktpa)	Sales (m$/y)
Acetic acid	617	1357	837	10%	617	13570	8373
Ethylene	1300-2000	200	260-400	0.2%	1100-1600	127000	140000-203000
Ethylene glycol	1300-1500	425	553-638	1.5%	900-1100	28000	25200-30800
Ethanol	815	71310	58141	93%	823	76677	63141
3-HPA	1100	0.04	0.04	100%	1100	0.04	0.04
Acetone	1400	174	244	3.2%	1,400	5500	7700
Acrylic acid	2688	0.3	0.9	0.01%	2469	5210	12863
Lactic acid	1,450	472	684	100%	1450	472	684
PDO	1760	128	225	100%	1760	128	225
BDO	>3000	3.0	9	0.1%	1800-3200	2500	4500-8000
Isobutanol	121	105	181	21%	1721	500	860
n-butanol	1890	590	1115	20%	1250-1550	3000	3750-4650
Iso-butene	>>1850	0.01	0.02	0.00006%	1850	15000	27750
Succinic acid	2940	38	111	49%	2500	76	191
Furfural	1000-1450	300-700	300-1015	100%	1000-1450	300-700	300-1015
Isoprene	>2000	0.02	0.04	0.002%	2000	850	1700
Itaconic acid	1900	41	79	100%	1900	41.4	79
Levulinic acid	6500	3.0	20	100%	6500	3.0	20
Xylitol	3900	160	624	100%	3900	160	624
FDCA	NA (high)	0.045	~10	100%	NA (high)	0.045	~10
5-HMF	>2655	0.02	0.05	20%	2655	0.1	0.27
Adipic acid	2150	0.001	0.002	0.00003%	1850-2300	3019	5600-6900
Sorbitol	650	164	107	100%	650	164	107
p-xylene	1415	1.5	2.1	0.004%	1350-1450	35925	48500-52100
Farnesene	5581	12	68	100%	5581	12.2	68
Algal lipids	>>1000	122	>122	100%	>>1000	122	>122
PHAs	6500	17	111	100%	6500	17	111

Table 3, prepared by researchers with the support of European Community [1], offers a comprehensive view of the present situation and highlights future trends. Bio-ethanol dominates largely, followed at by n-butanol (via A.B.E process), acetic acid and lactic acid. Xylitol, sorbitol and furfural derived from sugars also show significant markets, without petrochemical alternatives. A fast growing market has the succinic acid. The smallest bio-markets are those still in R&D phase, such as HPA, HMF, isobutene, isoprene, acrylic acid, and adipic acid. New products as FDCA, derivatives of levulinic acid and farnesene have still very high prices, but these could drop rapidly.

9. Conclusions

Renewable raw materials, namely the biomass, emerged recently as the future basis for the development of chemical process industries. The biorefinery concept ensures an optimal use of resources. A biorefinery is designed to supply a diversity of products from biomass, as biofuels, biochemicals, biopolymers, human and animal food products, as well as thermal and electrical energy. There are several types of biorefineries, classified by the type of feedstock, end-products and processing technologies. Lignocellulosic biorefinery is leading the development today. This new production model is compatible with the requirements of sustainable economy, primarily ensuring the recycling of CO_2 and of waste.

Because of the huge market, the manufacturing of biofuels is the key enabling factor for the development of biorefineries. Bioethanol is today one of the world's top chemicals. The first large scale plants for manufacturing second generation bioethanol are now on stream. FAME biodiesel remains a sustainable alternative to fossil diesel. The paper presents an efficient process by employing solid catalyst and novel reactor technology. New developments are the emergence of butanol as biofuel, and of farnasene as biodiesel. An intensive research takes place in the field of biotechnologies dealing with the use of algae for getting fuels and chemicals.

The manufacturing of biochemicals from biomass takes profit from specific building blocks. In contrast with petrochemical counter parts, these are actually more complex molecules containing already functional groups. The most interesting bio-building blocks today are methanol for getting olefins, ethanol for replacing fossil ethylene, glycerol, lactic acid, isobutanol, succinic acid, and levulinic acid. The paper presents the chemistry of the main valorisation routes.

The production of a new generation of polymers is a remarkable feature of the technologies based on biomass. Competitive-cost biodegradable polymers are now available, as PLA, PHA, and PHB. Petrochemical polyesters can be replaced in packaging and beverage bottles by polymers based on furan dicarboxylic acid (FCDA). On the other hand, olefin from biomass, as ethylene, propylene, isobutene and isoprene, can be used as drop-in feedstock in the existing manufacturing processes.

The development of technologies based on renewable raw materials should be not affected, at mean and longer term, by the emergence of shale oil & gas sources. On the contrary, a mix of biomass and fossil raw materials should ensure the feedstock basis over a long perspective. Projections estimate that around 2030 the share of biomass based chemical and fuel products should be 25 to 30%. This tendency could be accelerated because of the growing public awareness with respect to the threats raised by the climate change and the depletion of fossil resources.

The research and development in chemical technology has to ensure the scientific and engineering basis for this challenging enterprise.

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Profesorul Alexandre C. Dimian a obtinut titlul de Doctor in Ingineria Chimica la Universitatea Politehnica din Bucuresti (UPB) in 1977. Cariera universitara si stiintifica a debutat la UPB in anul 1967 in domeniul Ingineriei Reactiilor Chimice. Din 1982 a lucrat in industrie in calitate de consultant la Institutul Francez de Petrol (IFP) si s-a afirmat ca unul din pionierii in informatica aplicata in ingineria proceselor chimice din Europa, avind privilegiul de lucra cu cele mai avansate sisteme de calcul disponibile la acel timp pe plan mondial. A fost unul din primii creatori de programe de simulare pe PC, ca si de aplicare a simularii de proces in industrie. In paralel cu activitatea industriala, a continuat o sustinuta activitate de cercetare si publicare. A reinceput in 1993 o a doua cariera academica la Universitatea din Amsterdam din Olanda si apoi la Universitatea Tehnica din Eindhoven; a predat cursuri de proiectarea proceselor chimice, fiind responsabil pentru invatamint si cercetare in domeniul proiectarii si integrarii proceselor chimice; a devenit unul din principalii animatori in domeniul de Computer-Aided Process Engineering (CAPE) din Olanda si din Europa. S-a afirmat in domeniul ingineriei sistemelor chimice (Process System Engineering). A publicat peste 120 de lucrari in reviste de specialitate, 6 carti tiparite, din care 3 in Romania si 3 in prestigioasele edituri Elsevier si Wiley-VCH. Are lucrari citate in “biblia inginerilor chimisti” (Perry’s Handbook 6th & 7th editions) si este membru de onoare al Academiei de Stiinte Tehnice din Romania.

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RED AND GREEN ALGAE AS AN ALTERNATIVE FOR ETHANOL PRODUCTION. PRELIMINARY STUDY

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Abstract

Green and red algae are eukaryotic organisms that are found on the Black Sea coast in the warm period of the year, especially in sheltered areas, mainly on rocks and stones but also floating in the water. Climatic conditions, temperature, availability of sunlight throughout the day, nutrients from the water play an important role in the development of algal cultures. Macrophytes attracted scientists' attention because of the opportunities for valorization of the high content of polysaccharides stored. For this preliminary study, green and red algae have been used separately in bioethanol production. Biofuels made from algal biomass seem to have great perspectives due to high photosynthetic efficiency. Ethanol is produced by fermentation of carbohydrates, lignocellulosic materials, starches and represents an alternative energy source to fossil fuels. Continuing research done by other authors, we explored the possibilities of obtaining ethanol from algae in our specific area, by chemical hydrolysis and biochemical methods.

Key words: Algal biomass, Ethanol production

1. Introduction

Developed countries in the European Union look for exploiting and integrating the third generation biofuels obtained from biomass sources to replace the fossil fuels and maintain their energetical independence. Worldwide, the increasing demand for biofuels raised the issue of large area occupied, otherwise intended for food supplies. Algal biomass is a renewable source of high importance, which can be stored and operated on request without affecting food supplies.

Marine algae are considered „lower plants", being part of the thallophyte group and they form the large mass of the sea vegetation. Macrophytes are green, red or brown organisms living in the aquatic environment, especially in sheltered areas, mainly on rocks and stones but also floating in the water.Algae make thephotosynthesis process using the chlorophyll or phytocyanin pigment and they have an increased growth rate if the necessary conditionsfor development are

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fulfilled, such as: climatic conditions, CO_2, temperature, availability of sunlight throughout the day, nutrients from the seawater [1]. Macrophytes attracted scientists' attention because of the opportunities for valorization due to the high content of polysaccharides stored. Carbohydrate content can be converted into bioethanol by alcoholic fermentation. The protection of algae is absolutely necessary because they constitute a unique component of the aquatic biological balance andcan be an answer to the future society's problems in various fieldsas biology, medicine, chemistry etc.

Bioethanol can be produced from any biological feedstock containing appreciable amount of sugar or material that can be converted into sugar such as starch or cellulose. Bioethanol is mainly converted into bio-ETBE or used mixed with gasoline and diesel [2].

Several studies had been performed in the past for obtaining ethyl alcohol and other biofuels from algae. Gupta et al. [3] investigated the possible use of *Saccharomyces cerevisiae*VITS-M_2 (yeast culture) for ethanol production using the carbohydrates extracted from marine algae. The fermented product was distilled using a model distillation unit and measured qualitatively using HPLC chromatography. The confirmation of ethanol presence was performed by litmus, iodoform and ester tests. Lou et al.[4] studied the ethanol productionfrom CO_2 and water via an intracellular photosynthetic process in microscopic blue-green algae, excreted through the cell walls, collected from closed photo-bioreactors as a dilute ethanol-in-water solution, and purified to fuel grade ethanol. Also, Ellis et al. [5] studied the ethanolicfermentation by*Clostridium saccharoperbutyl-acetonicum*N1–4 using wastewater algae biomassfrom the Logan City Wastewater Lagoon system.

The biomass usage will increase significantly in the upcoming years and there is no consensus on the maximum level biomass exploitation that could beachieved [6]. However, numerous barriers remain to be overcome before the large-scale production of algae-derived biofuels become a commercial reality. Producing low-cost algal biofuels requires improvements in algal biology through metabolic engineering to achieve “optimum” attributes such as high growth rate and ease of extraction[7].

A scientific report [8] showed that some macrophytes on Black Sea shore have a high content in carbohydrates (48.5-55% wt, related to the dry matter), this is why they can be taken into consideration as raw material for bioalcohol production.

Continuing the research done by other authors, we explored the methodsfor obtaining bioethanol from three types of marine algae intwo main ways: chemical treatment and biochemical treatment.

2. Materials and methods

Raw materials for fermentation were three species of macrophyte algae common for the Black Sea shore: *Ulvalactuca*, *Ceramiumvirgatum* and *Cladophoravagabunda*(Figures 1-3).

Fig.1.*Ulvalactuca* – aspect of the natural environment

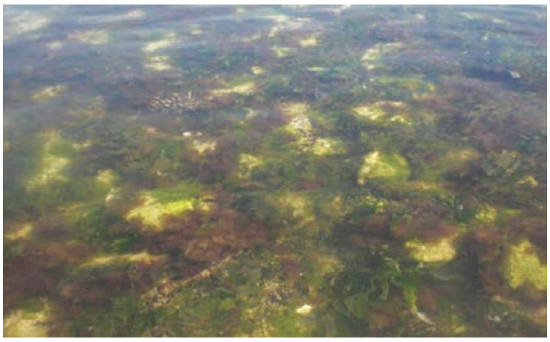

Fig.2. Stoney substrate populated by *Ceramiumvirgatum*epiphytic on*Ulvalactuca* species

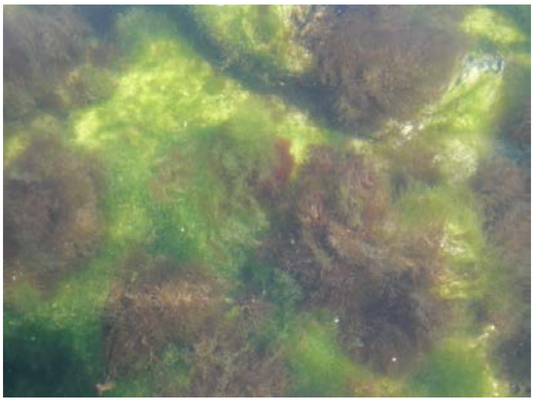

Fig.3. Abundant development of*Cladophoravagabunda* species in the summer

They were harvested separately, washed with distilled water, drained and used in fresh state. The moisture content of the plants depends on the harvesting time of the year and on the method used to measure it. Classically, the moisture content is determined by drying the biomass at 105 ^{o}C for hours to constant weight. We preferred to use a thermobalance, the moisture analyzer OHAUS, model MB45, programmed in the following steps: 7 minutes at 200 ^{o}C, 1 minute at 150 ^{o}C and 12 minutes at 105 ^{o}C, as recommended for wet vegetables, by the supplier. The measured moisture content in these conditions was: 84.55± 0.6% for *Ulvalactuca*, 72.78%±0.03% for *Ceramiumvirgatum* and 84.70 ± 0.15% for *Cladophoravagabunda*.

As a reference substance for alcoholic fermentation, microcrystalline cellulose powder, 20 µm, was used, a reactive from Aldrich.

Cellulase for the biochemical treatment of cellulosic material was powder off-white from *Aspergillusniger* produced by Aldrich, with 1.14 U/mg.

In some fermentations, germinated barley from S.C.MadalBal trading Romania SRL, produced by ZöldForás was used as a saccharificationagent.The concentration of alcohol in the fermentation broth was determined following the Romanian standard method SR 184-2, with the Glass-CHEMapparatus, Model OH-1 (Figure 4). The method consists in the batch distillation of the broth sample, with the azeotrope ethanol-water distilling first, followed by water. The distillation product is collected in a picnometer and the ethanol concentration is calculated by correlation with the ethanol- water mixture density.

Fig.4. Oenologic equipment for alcohol concentration determination

3. Experimental

Different ways to obtain alcohol from algae were studied, in order to chose the more appropriate one for the next optimization study.

Two main ways for the cellulosic material decomposition were investigated: acid hydrolysis of polysaccharides and the biochemical treatment with cellulase. Under any of these treatments, polysaccharides are broken into smaller molecules some of them being reducing sugars from which alcohol is obtained in an alcoholic fermentation process. For the biochemical treatment, besides the cellulase, there were trials with and without a supplementary saccharification agent, the powder of germinated barley. The description of these methods is given as follows:

a) Acid hydrolysis of polysaccharides followed by ethanolic fermentation

200 mL of fresh algae were washed with distilled waterand then separated by centrifugation at 1500 rpm for 10 minutes. The algae were hydrolyzed during 48 hours in 200 mL distilled water, by adding 2mL of concentrated H_2SO_4, thus transforming polysaccahrides in reducing sugars. Then, the samples were neutralized with $BaCO_3$ and centrifuged again at 1500 rpm for 10 minutes, for separating the aqueous extract from algae. The sugars extract is processed in anaerobic fermentation, at dark, with yeast (3-4 g), for 72 hours, at room temperature (26^{o}C). The obtained solution is filtered and analyzed with the oenologic equipment for alcohol concentration.

b) Biochemical treatment of algae with cellulase, green barley and ethanolic fermentation

For the experiment, 320g of *Ulvalactuca* was washed withdistilled water. The algae were boiled in 1200 mL distilled water during 15 minutes. The solution is cooled down at 40-45^{o}C and 1 gram of cellulase (total 1140 units) is added. After 48 hours, the system is reheated to boiling. After cooling at 50-60ºC, 5 g of germinated barley (powder) is added.When reaching 30ºC,1 g of yeastwas added.The mixture is also kept in the dark, in the absence of oxygen for 48 hours. The concentration of ethanol in the broth is measured.

The ethanolic fermentation was carried out similarly with 8,2 g cellulose in 450 mL water.

c) Biochemical treatment of algae with cellulase and ethanolic fermentation, with algae included

The three types of algae were boiled separately in distilled water for 20 minutes. After cooling at 40-45ºC, 1g of cellulasewas added. The pH was adjusted to 5-6. The mixture is kept 48 h in order to polish the polysaccharides conversion to reducing sugars, then in the dark, for 48 other hours in the absence of oxygen, for alcoholic fermentation at room temperature (29^{o}C), with 1 g of yeast. Algae were present in the broth during the whole treatment.

The same procedure was applied to cellulose (8.2 g in 450 mL water) with 0.5 g, 1 g and 2 g of cellulase, respectively, in order to determine the optimum quantity in the process. The pH was naturally 6.

d) Biochemical treatment of algae with cellulase and ethanolic fermentation, with algae separated after cellulase treatment

The previous treatment (*c*) was applied with the difference of separating the algae from solution after the cellulase treatment. This procedure was tried in parallel with procedure*c)* to find if the cellulosic material decomposition would continue during the alcoholic fermentation or not.

4. Results and discussion

The results obtained through the studied methods in terms of ethanol yield related to the dry matter are shown in Table 1. Taking into account that carbohydrates constitute about half of the dry matter, the yields related to the carbohydrates are double and in this study, they are pretty high. The most productive is *Ulvalactuca* and the least is *Ceramiumvirgatum*.

Table 1.

Yield of ethanol obtained from algae or cellulose through different methods

Method	Type of algae/ cellulosic material	Yield of ethanol related to dry matter (DM)
I. Acid hydrolysis of polysaccharides followed by ethanolic fermentation	Ulvalactuca	9.1 %
	Ceramiumvirgatum	7.4 %
	Cladophoravagabunda	7.8 %
II. Biochemical treatment with cellulase, barley and ethanolic fermentation	Ulvalactuca	6.51 %
	Cellulase	9 %
III.Biochemical treatment with cellulaseandethanolic fermentation with algae included	Ulvalactuca	20.45 %
	Ceramiumvirgatum	7.01 %
	Cladophoravagabunda	16.06 %
	Cellulase	40.73%
IV. Biochemical treatment with cellulaseandethanolic fermentation withseparatedalgae	Ulvalactuca	21.0%
	Ceramiumvirgatum	8.1%
	Cladophoravagabunda	9.15%

As one can see, the acid hydrolysis of polysaccharides followed by ethanolic fermentation gave smaller yields in ethanol comparing with the biochemical treatments, excepting the second treatment, with barley. That treatment was only tested on *Ulva* and cellulose because of momentarily lack of *Ceramium* and *Cladophora* and it was abandoned later because of the weak yields even on cellulose.

The third and the fourth ways give comparable results, except *Cladophora* giving better results when kept in contact with the fermentation broth in alcoholic fermentation.For the *Ulva*, keeping the algae in the broth along the entire process doesn't lead to great improvement in alcohol yield and the separation of algae after the saccharification process would be preferable for easier control of the alcoholic fermentation process.

The alcohol yield obtained by biochemical treatment of *Ulvalactuca*is strikingly higher than from the other algae and this is probably due to the predominance of cellulose in the lignocellulosic material in *Ulva*, by comparison.

The alcohol yield obtained from pure cellulose as reference substance in the biochemical treatment is very high, 40.73% comparing with the theoretical maximum of 47.9%, following the stoechiometry of the reaction:

$$C_6H_{12}O_6 \rightarrow 2\ CH_3\text{-}CH_2\text{-}OH + 2\ CO_2$$

This suggests that the chosen treatment is effective and this will be the way for the following experiments.

Finally, three experimental determinations took place following the third pathway with the reference substance (8.2 g cellulose) and different quantities of cellulase: 0.5 g, 1 g and 2 g respectively 570 U, 1140 U and 2280 U. The results of these determinations are shown in Figure 5.

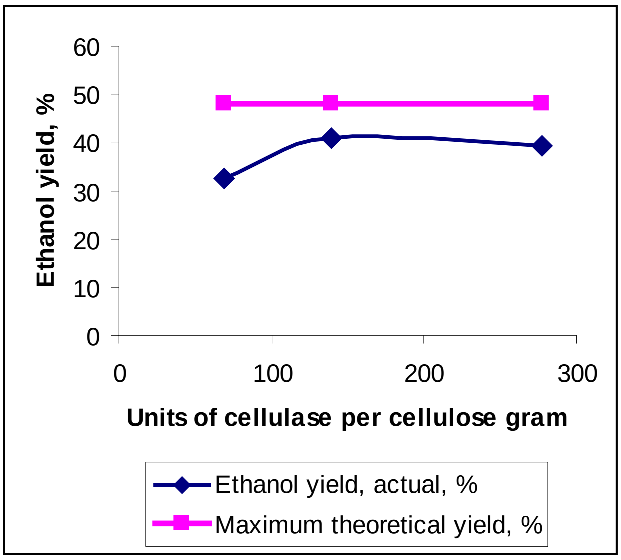

Fig.5. Influence of cellulase quantity on the ethanol production

The results indicate the increasing of ethanol production up to 140U/g cellulose, and a limitation to approx.40% of ethanol yield afterwards, this meaning 83% from the theoretical yield.

5. Conclusions

The preliminary study has shown that alcoholic fermentation of green and red algae is feasible. The results were better forbiotreatment with cellulase comparing with the acid hydrolysis.

The higher yield of ethanol was obtained from *Ulvalactuca*(20-21 %wt, related to the dry matter), this indicating that species to be considered as raw material for an industrial process.

For a future experiment, it will bechosen thebiotreatment with cellulase followed by separation of algae and then the alcoholic fermentation, also searching for a cheap method to produce cellulase and improving the process parameters.

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INFLUENCE OF ELECTROMAGNETIC RADIATION ON MICROALGAE GROWTH

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Abstract

There is some information on the bio-effects of microwaves on microalgae. Some recent studies demonstrates that samples exposed to microwave of various powers showed significantly higher growth rates and biomass concentration than non-irradiated controls. The aim of this study is to investigate the influence of microwave radiation on growth rates, biomass concentration and oil content of Nannochloris sp. microalgae. To perform this experiment five microwave treatment conditions were established, using five microwave power values (140, 220, 300, 400 and 500 W), and each experiment was performed for 10 seconds. The results obtained had shown that the samples exposed to microwave irradiation have a higher concentration biomass and growth rate compared to non-irradiated controls.

Key words: Microalgae, microwave treatment

1. Introduction

The biodiversity of microalgae is enormous and represents an almost untapped resource [1]. Because of their capacity to produce a high quantity of biomass in short time and a superior yield of oil per hectare compared to the traditional crops, the microalgae have attracted interest in the last few years [2]. Until now most of the literature studies were focused on the growth of microalgae for biodiesel production [3], for reducing emissions of a major greenhouse gases, because microalgae are capable of fixing a high quantity carbon dioxide (1 kg of dry algal biomass requires about 1.8 kg of CO_2)[4]. Some species of microalgae, especially salt water species, are used because of their high content in polyunsaturated fatty acids (PUFA) [5].

The ability of microalgae to adapt their metabolism to varying culture conditions provides opportunities to modify, control and, thereby, maximize the

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formation of target compounds [6]. Given this characteristic of the microalgae, the aim of this study is to maximize the production of biomass using microwave (MW) treatment.

Microorganisms are regarded as one of the best test systems for the probing of the MW exposure because of their rapid growth rate and the existence of an array of experimental designs and testing protocols available for the elucidation of MW-induced effects [7].

Microwave bio-effect on microorganism has been investigated in the past in few papers. The first time it was investigated the growth rate of yeast *Saccharomycescerevisiae*, *Candida albicans* after microwave treatment at different frequencies [8, 9]. Asadi et al (2011) found that growth rate and biomass accumulation of *Phormidiumsp*. was highly influenced by different microwave treatments [10].

2. Experimental

2.1. Microalgae strain and culture medium

Nannochloris sp. 424-1 is a strain deposited under number CCAP 251/10 in the Culture Collection of Algae and Protozoa (CCAP) at the Scottish Marine Institute, Aryll, UK[11]. The culture medium for *Nannochlorissp.* was Zarrouk medium, with the following composition (g/L) 16.8 $NaHCO_3$, 0.5 K_2HPO_4, 2.5 $NaNO_3$, 1.0 K_2SO_4, 1.0 NaCl, 0.2 $MgSO_4.7H_2O$, 0.04 $CaCl_2.2H_2O$, 1 mL/L of trace metal solution, and 5 mL/L of chelated iron. Before use the culture medium was sterilized at 121 °C, 15 min using an autoclave.

2.2. Cultivation

Microalgae were cultivated in 250mL Erlenmeyer flasks containing 230 mL Zarrouk medium and 20 mL inoculum of Nannochloris sp. The flasks were incubated at constant temperature (28°C) and constant stirring rate (200 rpm), using an incubator Innova® 42Incubator Shaker Series from New Brunswick Scientific. All the flasks were continuously aerated with a synthetic gas mixture containing 7% CO_2, 14% O_2 and 79% N_2 (v/v) and illuminated using two fluorescent lamps at a light intensity of 250 $\mu E/m^2/s$. The initial cellular concentration for each experiment was set to 1.66×10^7 cell mL^{-1} (day 0), using manual cell counts on a ThomaHemocytometer. The samples were incubated for 3 days.

2.3. Microwave treatment

For the microwave treatment, six Erlenmeyer flasks with microalgae cultures were used. Five samples were used for microwave treatment and one flask was used as a blank sample. The cultures were microwave-treated after 24 h of incubation (day 1), at a frequency of 2450 MHz, using a modified commercial Samsung oven (850 W) and combining two variables: time of treatment (10 seconds) and the microwave power value (140, 220, 300 W, 400W and 500W). All the samples were continuously stirred at 400 rpm during the microwave treatment to ensure uniform distribution of the temperature in the samples. After the treatment, all the samples were kept in the incubator in the conditions described above for 48 h (2 days).

2.4. Dry biomass quantification

The quantity of the algal biomass obtained per mL of sample was determined by measuring the dry weight. Three days (56h) after inoculation the microalgae were harvested by centrifugation at 8000 rpm for 10 minutes using a Rotina 380R centrifuge from HettichZentrifugen. The biomass obtained was dried using the standard method [12].

3. Results and discussions

In Fig.1, the number of cells obtained in function of incubation day was plotted. It can be noticed the beginning of a growth curve for all the micro-treated samples. All these samples presented an increase of the cells concentration from the first day after the treatment with microwave. A higher increase of the cell number is observed for the samples microwave-treated at low microwave power (140, 220, 300W). For the samples exposed to higher microwave power, adecrease in cell number can be observed, but these samples still showed an increase compared with the control sample.

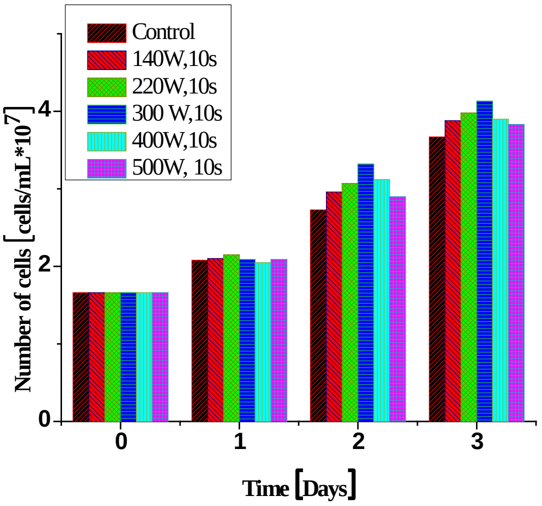

Fig. 1. The effects of various microwave treatment on the cell number for *Nannochlorissp* culturesin each day of incubation

Effects of microwave treatment on *Nannochloris sp.* biomass concentration are showed in Fig.2. All the microwave-treated samples presented an increase of the dry biomass compared with the control sample. The results obtained are in concordance with the results for cell concentrations. The maximum concentration, expressed as dry biomass/mL, was ~0.93 mg/mL and was obtained for the sample treated at 300W. The increase compared with the control sample expressed in percentage was ~38%.

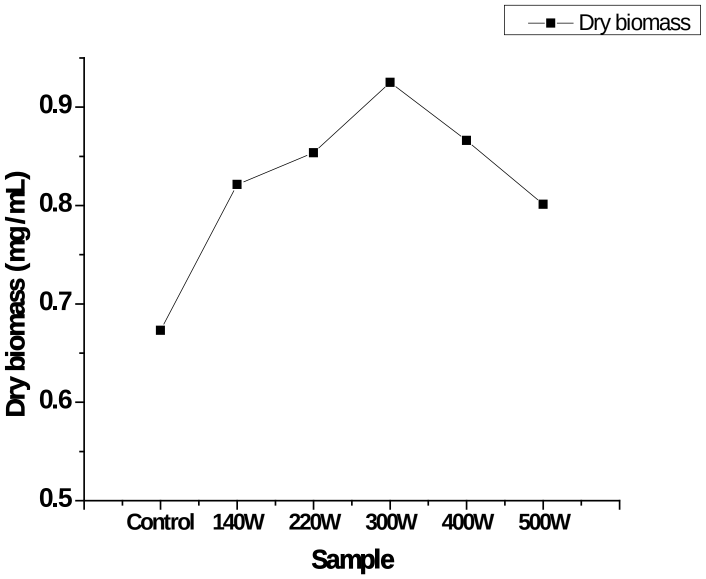

Fig. 2. The effects of various microwave treatment on dry biomass amount of microalgae *Nannochloris sp.*

4. Conclusions

Data obtained in this study revealed that microwave treatment induced a specific metabolic activity to microalgae cultures. In this case, all the samples microwave-treated presented an increase of the number of cells and of the biomass concentration compared with the control sample. These results represented just a support for our future work. The experiment will be continued by incubating the samples after irradiation until the growth rates will reach the stationary growth phase. It also conducts a study on influence of microwave treatment on the oil content.

Acknowledgements

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ADSORPTION OF CRUDE OIL USING BIOSORBENTS IN ACCIDENTAL OIL SPILLS

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Abstract

Nowadays the pollution control and management is a high priority, mostly because the pollutants presented in water, adversely affect human and animal life. When oil comes in contact with water, it forms of oil-in-water emulsion or floating film that needs to be removed before it is discharged into the environment. In contact with water the physical and chemical properties of oil changes progressively. Equipments used for cleaning and recovery from an oil spill includes: booms, skimmers, chemical and biological agents, sorbents, bioremediation agents, vacuums, shovels and other road equipment, typically used to clean up oil on beaches.

Naturally available low cost sorbents have gained importance as effective alternative to conventional sorbents, to be used in oil spills. Persistent Organic Pollutants (POPs) have been and continue to be one of the greatest environmental concerns worldwide. POPs and heavy metals are very dangerous for health because of their bio-accumulation and bio-magnification potential in aquatic food web. Recently attention has been diverted towards the biomaterials which are by-products, or the wastes from large-scale industrial operations and can be used as sorbents. Use of natural sorbents for remediation of the consequences of such accidents is promising and deserves attention, because they are very efficient, available and eco-friendly. In this research, peat moss, sunflower seed cake, sunflower hulls and polypropylene were used for crude oil sorption. Also, in this study three specific pollutants were used: waxy crude oil, crude oil asphaltenes, crude oil type B (semi-waxy crude oil) and light vacuum oil.

The results presented and discussed in this work pointed out that the tested sunflower seed cake and sunflower hulls, by-products of oil refining, are a new biodegradable sorbents, cheap, effective, with average sorption properties and may be considered an excellent potential sorbent to be used in oil spills on inland, oceans and beaches. The sunflower hulls also showed very good buoyancy. The major advantages of biosorption over conventional treatment methods include low cost, high efficiency, minimization of chemical or biological sludge and possibility of metal recovery. The aim of this work is to investigate sunflower hulls, sunflower seed cake and peat moss as potential natural materials for the oil spills.

Key words: oil retention, natural sorbent, oil spills, buoyancy, adsorption

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1. Introduction

We know that oil is one of the most important sources of energy in the modern industrial world. During transportation, the chance of oil spillage over the water body occurs due to accidents or by deliberate action during war time which causes environmental pollution.

Oil sorbents have been extensively used for remediation (cleanup and recovery) of the consequences of such marine accidents.

Sorbents made from structured fibre assembly are found to be the best materials to clean up oil spills [1]. The use of sorbents made from organic materials does not cause additional problems in the disposal of the spilled oil. In normal situations the biomaterial is used in a coastal bio power plant, but new recovery technologies of petroleum show the possibility of production of bio fuel from the used organic sorbent materials by extraction.

The major advantages of biosorption over conventional treatment methods (booms, skimmers, vacuums, shovels etc.) are low cost, high efficiency, minimized chemical and biological sludge and regenerability.

The oil sorption and retention behaviour of sorbents are influenced by the material and structure of the sorbents, oil physical characteristics, the temperature of the water (affecting evaporation and biodegradation) and the type of oil spilled [2]. For sustainable environment the disposal of used sorbents is a major issue. The aim of this study is to compare the adsorption capacity of sunflower seed cake and sunflower hulls with polypropylene and peat moss.

The first goal of the research was to acquire an understanding of adsorption process and other important preliminary information (the characteristics of an ideal sorbent material used for oil spill cleanup). The second goal was to evaluate the:

- sorption capacity;
- the capillary ascension of sorbents;
- the recovery of petroleum products by extraction;
- the buoyancy;
- the sorption from a solid stone.

2. Fibre materials used for oil sorption

2.1. Seed cake sunflower

Sunflower seed cake (an agricultural by-product) is a low cost and easily available material which can be an alternative adsorbent for more costly adsorbents [2, 3]. This fibrous by-product of oil extraction (lower in energy value and lysine), is a cheap source of high quality protein and fibre and is frequently utilized in animal nutrition.

The production of sunflowers is increasing in Ukraine (11.05 million metric tons) and Russian Federation (10.53 million metric tons of sunflower seed). Currently Romania occupies the fifth place in the production of sunflowers (2.2 million metric tons) [5].

The peat moss and polypropylene are the most used sorbents, but also sunflower seed cake could be one of them.

The sunflower oil extraction industry produces 3 kinds of meal (cake), presented in Figure 1.

- Type 1: Meal produced from un-hulled seeds, containing around 28% protein and 25%-27% fibre (Figure 1-a, 2);
- Type 2: Meal produced from partially de-hulled seeds, containing 34%-37% protein and 18% fibre (Figure 1-b);
- Type 3: Meal produced from seeds with 2-step de-hulling process, containing 40%-42% protein and 12%-14% fibre (Figure 1-c);

a ***b*** ***c***

Fig. 1. Sunflower seed cake, a- type 1, b-type 2, c- type 3

Fig. 2. Biodegradable natural sorbent – sunflower seed cake type 1 from S.C. TIMEX SURVEYOURS S.R.L.

A. Ş. Yargiç, R. Z. Yarbay Şahin and others [4] analysed the sunflower seed cake. The preliminary analysis indicated that sunflower seed cake (SSC) have

7,72% moisture, 6,71% ash, 75,15% volatile and 10,95% fixed carbon content. They also found that SSC consist of 33,12% lignin, 12,53% cellulose, 10,92% hemicelluloses, 22,90% holocellulose, 23,59% extractive material and 30,30% oil, by structure analysis. The physical morphologies and surface properties of SSC were examined by using a scanning electron microscopy technique (SEM). In Figure 3 there is shown SEM image of SSC.

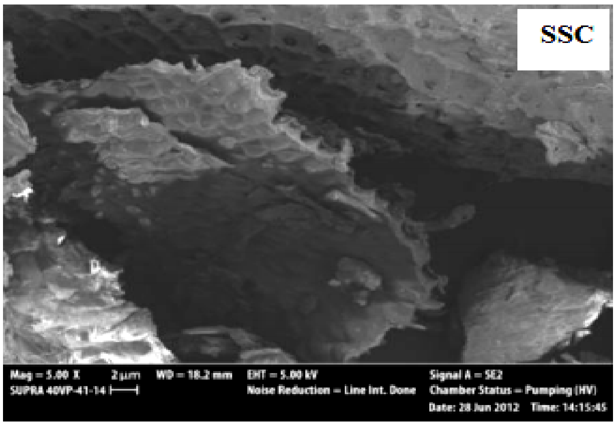

Fig. 3. SEM image of sunflower seed cake [4]

2.2. *Sunflower hulls*

Sunflower hulls are the by-product of the de-hulling of sunflower seeds before they are used for oil extraction. Sunflower seeds contain about 20-30% hulls that are often removed before oil extraction due to their deleterious effects on oil presses and because they reduce the quality of both oil and meal (Kartika, 2005). Sunflower hulls (Figure 4) are light in weight and bulky, which promotes its buoyancy. De-hulling is done after cleaning the seeds and drying them down to 5% moisture [6].

Fig. 4. Biodegradable natural sorbent – sunflower hulls

2.3. Polypropylene fibre

Synthetic sorbents such as polypropylene (Figure 5, 6) and polyurethane are the most commonly used commercial sorbents in oil-spill cleanup, due to their oleophylic and hydrophobic characteristics. A principal disadvantage is that they degrade very slowly as compared to the mineral or vegetable products. The limitations of the inorganic mineral products and organic synthetic products have led to the recent interest in developing alternative materials, especially biodegradable such as: cotton, wool fibres, sugarcane bagasse, sunflower seed cake etc [7].

The oil sorption of polypropylene is through capillary bridges between fibres. So it is entirely based on porosity and structure of the sorbent materials.

Fig. 5. Synthetic sorbent- shredded polypropylene from S.C Envirotech S.R.L.

Fig. 6. Polypropylene adsorbent mats from S.C. OIL DEPOL S.R.L

2.4. Peat moss

Peat is a natural material which contains lignin and cellulose as major constituents and has been studied as a sorbent by various researchers, which suggested that the peat without any treatment has a low capacity of adsorption (16.3 mg/g on particles of size 150-200 μm) [8,9].

Peat moss is a non-toxic, all natural, 100% organic, industrial adsorbent that is economical, efficient, non-abrasive and in its natural state is already biodegraded. The peat (the manufacturers call it “Environmental Intelligence”) is available in compressed and loose-filled bags, in booms, socks, cushions and pads, in various combinations of spill kits and in customized filtration and bioremediation treatment packages.

Fig. 7. Peat moss-based (Petroads) biodegradable oil adsorbant

Peat moss (Figure 7) should be scattered across the surface of the polluted water to a sufficient depth so as to ensure that full adsorption will take place. The adsorption capacity of peat in removing various types of pollutants varies a lot depending on peat origin, degree of decomposition, particle size, metal concentration, ligand concentration and competing ions.

3. Results and discussion

Tests were carried out on several groups of poly-dispersed sorbents such as peat moss, polypropylene, sunflower seed cake and sunflower hulls. The peat moss and polypropylene used were taken from the company S.C. OIL DEPOL S.R.L. (one of the most important depollution company in Romania) and the sunflower seed cake was taken from the company S.C. TIMEX SURVEYOURS S.R.L., Romania. The densities of the four tested pollutants are presented in Table 1 and the apparent density of the used sorbents in Table 2.

To observe the sorption performances of the used sorbents, two sets of experiments were performed as follows:

A. Determination of adsorption capacity on the basis of the standard F716-09;

B. The behaviour of sorbents in the water-oil mix.

Table 1.

The properties of the pollutants studied

Pollutant type	Density of 23°C [kg/m^3] SR EN ISO 12185:2003
Asphalt crude oil from „Potlogi”	843.4
Waxy crude oil from „Ochiuri”	842.7
REBCO crude oil (type B)	860.1
Light vacuum oil	890.0

Table 2.

The density of the sorbents used

	Polypropylene	Peat moss	Sunflower seed cake type 2	Sunflower hulls
Density Kg/m^3	72.6	80	1055	130.5

3.1. Test methods for oil sorbents

3.1.1. Test for sorption capacity

The first experiment was conducted with petroleum products and sorbents, at a constant working temperature (23ºC). Since testing experiments are done in the laboratory, they could not simulate external parameters that influence the evolution and evaporation of pollutants in nature (heat transfer processes at the interface oil-air, sea currents, wind etc.). A mixture of REBCO crude oil and sorbent (sunflower seed cake „SSC”) are illustrated in Figure 8.

For the first experiment, 50 mL of crude oil was poured into three 250 mL beakers and then 5 g of sorbent was added. These tests were performed in a static system, without stirring. After 20 minutes, the content of the beakers was drained for 20 seconds. After this, the sorbent was removed from the beakers and their weight was measured (Figure 9-12).

Fig. 8. Rebco crude oil adsorbed by SSC

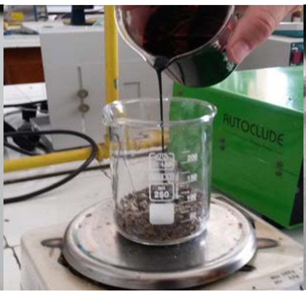

Fig. 9. Waxy crude oil adsorbed by SSC

Fig. 10. Light vacuum oil adsorbed by SSC

Fig. 11. The behaviour of SSC in contact with the three analysed crude oils (Rebco crude oil, waxy crude oil and asphalt crude oil)

Fig. 12. The behaviour of the four sorbents analysed in contact with light vacuum oil

A first goal of the research was to estimate the sorption capacity of these adsorbents. The adsorption tests were performed to determine the amount of liquid adsorbed by the adsorbent, the results are given in Table 3. As it can be seen, the sorption capacity of the sorbents followed the general trends: polypropylene > peat moss > sunflower seed cake > sunflower hulls. In comparison with the peat moss and polypropylene which are used in the marine depollution, sunflower seed cake type 1 and sunflower hulls gave good results.

*Table 3***.**

Specific retention of oil products on various adsorbents after 20 min., at a working temperature of 23°C

Adsorbant	**Oil sorption capacity REBCO** **weight of adsorbed oil/weight of sorbent (g/g)**	**Oil sorption capacity WAXY CRUDE OIL** **weight of adsorbed oil/weight of sorbent (g/g)**	**Oil sorption capacity ASPHALT CRUDE OIL** **weight of adsorbed oil/weight of sorbent (g/g)**	**Oil sorption capacity LIGHT VACUUM OIL** **weight of adsorbed oil/weight of sorbent (g/g)**
Sunflower seed cake TYPE 1	2.601	2.800	2.834	3.300
Sunflower hulls	1.801	1.827	2.234	2.210
Peat moss	3.450	3.151	3.086	3.050
Polypropylene	6.808	6.716	6.633	4.903

The graph of petroleum products adsorption on different type of sorbents is presented in Figure 13.

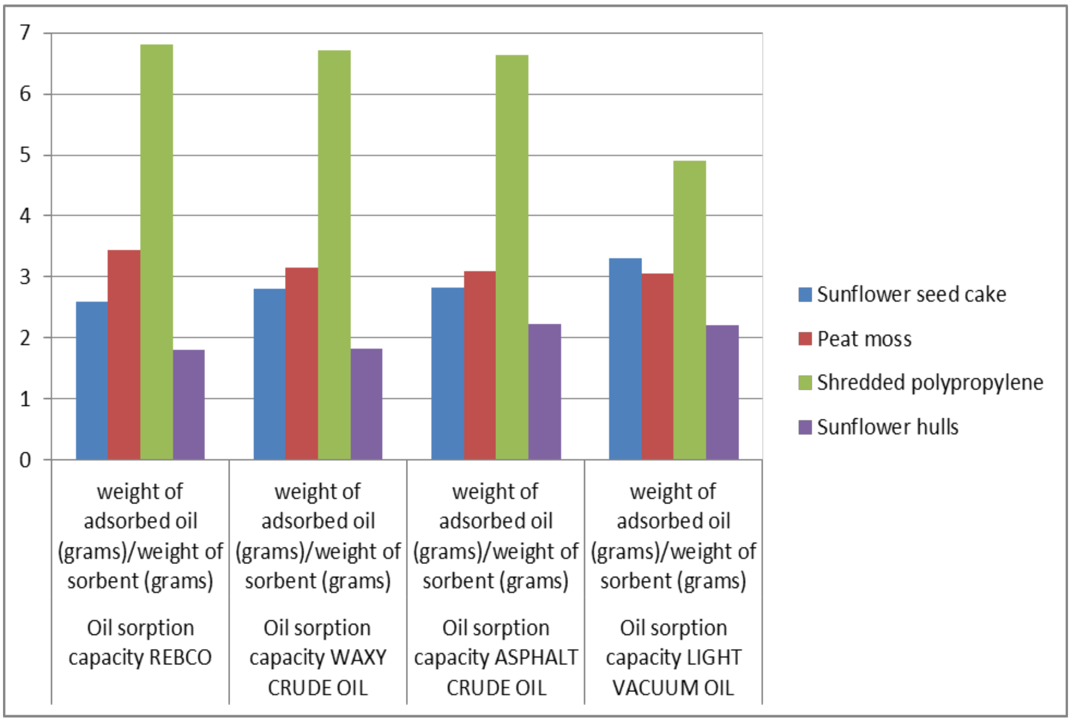

Fig. 13. The graph of petroleum products adsorption by sorbents

3.1.2. Capillary ascension tests

We have tested the kinetics of the capillary action of liquid in the pores of the natural sorbents analysed (peat moss, sunflower seed cake and sunflower hulls). The column used had a diameter of 1.7 cm, and 12 cm in length and is illustrated in Figure 14.

Fig. 14. The column used for tested the capillary ascension of sorbents

We poured REBCO crude oil, waxy crude oil, asphalt crude oil and vacuum light oil (75 ml) in three separate Berzelius beakers and then we introduced the columns packed with natural sorbents, peat moss, sunflower seed cake and sunflower hulls (up to 4 cm) in each beaker. Adsorbent suction power was calculated by measuring the amount of oil adsorbed at precise time intervals (15, 30, 60, 120, 300 and 1800 seconds) [7]. The results are shown in Table 4, 5, 6 and in Figure 15, 16, 17.

This test reveals the phenomena of adsorption by capillary action, phenomena that occur on removal of petroleum products from the affected environment.

Table 4

The kinetics of retention in the pores of peat moss

Time (s)	Rebco crude oil adsorbed (g)	Waxy crude oil adsorbed (g)	Asphalt crude oil adsorbed (g)	Vaccum light oil adsorbed (g)
15	4.00	2.85	2.00	1.60
30	4.60	3.60	3.00	2.00
60	4.70	3.40	3.30	2.40
120	4.80	3.90	3.50	2.60
300	4.85	4.00	3.80	2.80
1800	5.00	4.50	4.10	2.80

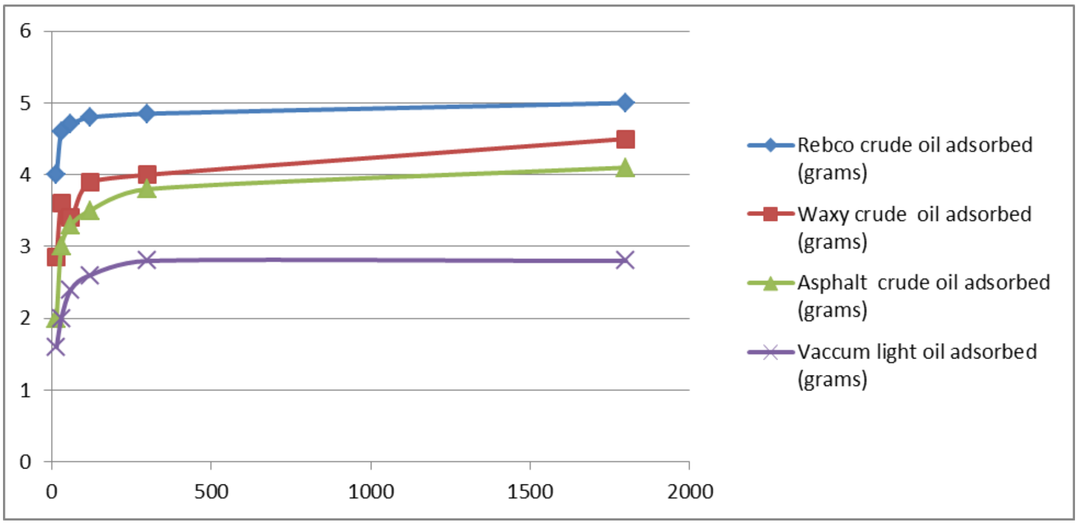

Fig. 15. Curves of oil sorption kinetics on peat moss

Table 5

The kinetics of retention in the pores of sunflower seed cake

Time (s)	Rebco crude oil adsorbed (g)	Waxy crude oil adsorbed (g)	Asphalt crude oil adsorbed (g)	Vaccum light oil adsorbed (g)
15	2.00	2.10	2.00	1.55
30	2.65	2.30	2.50	1.60
60	2.80	2.70	2.80	1.70
120	2.90	3.00	3.00	1.85
300	3.20	3.15	3.30	1.90
1800	3.65	3.50	3.47	2.70

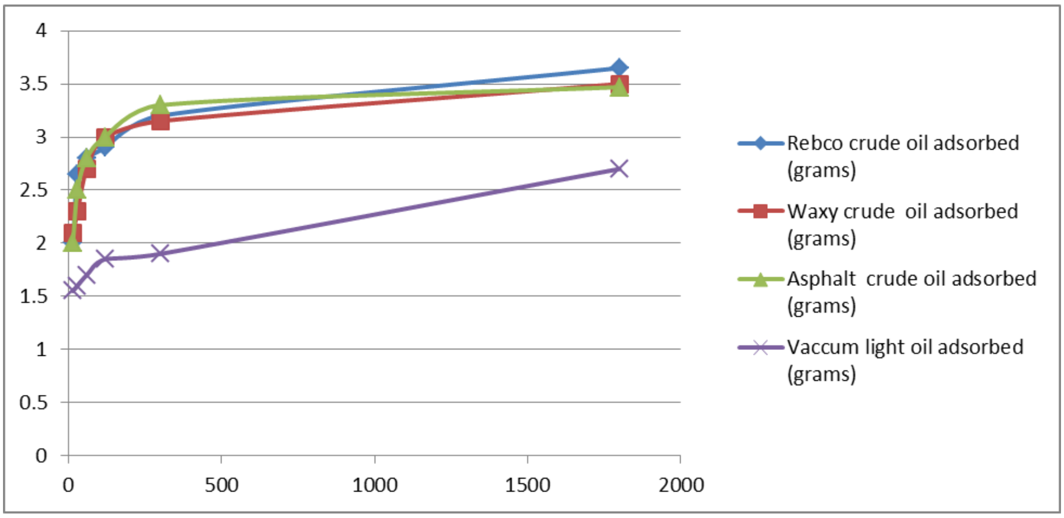

Fig. 16. Curves of oil sorption kinetics on sunflower seed cake type 1

Table 6.

The kinetics of retention in the pores of sunflower hulls

Time (s)	Rebco crude oil adsorbed (g)	Waxy crude oil adsorbed (g)	Asphalt crude oil adsorbed (g)	Vaccum light oil adsorbed (g)
15	1.65	1.40	1.50	1.00
30	2.40	1.35	2.00	1.30
60	2.55	1.40	2.60	1.50
120	2.60	1.70	2.80	1.80
300	2.70	2.00	2.85	2.50
1800	2.95	2.90	2.95	2.85

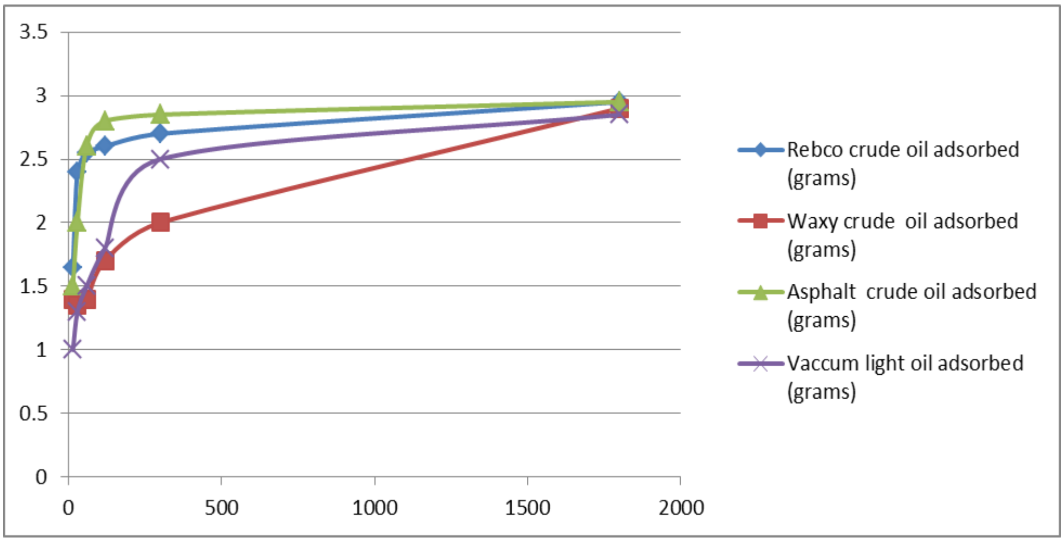

Fig. 17. Curves of oil sorption kinetics on sunflower hulls

In the case of crude oil, the retention time is comprised within the interval of 15s to 1800s. Due to increased intrinsic capillary action, peat moss encapsulates the petroleum products faster.

3.1.3. Test for recovery of adsorbed oil

a. Thermal method

These methods have the basic principle of extraction and destruction of pollutants by subjecting the contaminated material with thermal methods at high temperatures. The apparatus used to recover pollutants in this study is illustrated below (Figure 18).

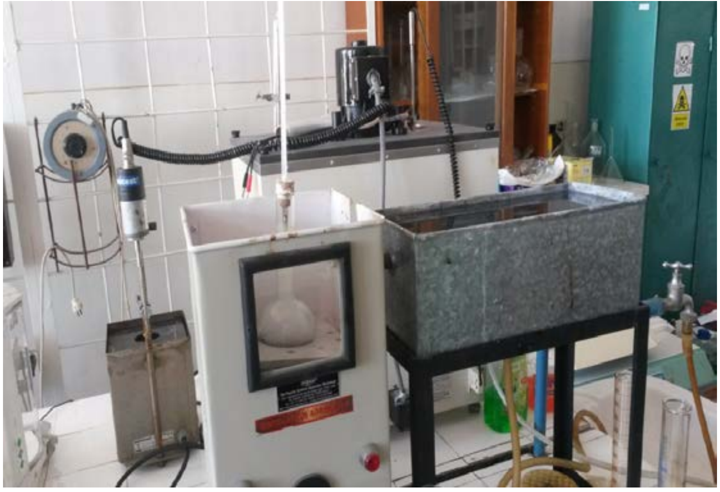

Fig. 18. The extraction of crude oil from sunflower seedcake soaked by Rebco crude oil

Fig. 19. The mixture of sunflower seed cake with waxy crude oil

For this experiment (Figure 18, 19), 10 g of sunflower seed cake was weight which adsorbed 4.29 g of waxy crude oil. The waxy crude oil soaked by the sunflower seed cake (14.29 g) was poured in an 100 mL volumetric flask. The initial temperature was 26^0C. The first drop was recovered at 94^0C. The extraction took approximately 20 minutes at 95-96^0C. After 20 minutes, the recovered oil was weighed. The amount of petroleum product recovered from the sunflower seed cake soaked by waxy crude oil was 2.68 g (62.47%).

The experiment was repeated for sunflower seed cake soaked by Rebco crude oil. The procedure was the same. The mixture of sunflower seed cake and the Rebco crude oil weighted 16.22 g. After 20 minutes the oil recovered was weighted. The amount of oil recovered from the sunflower seed cake soaked by Rebco crude oil was 3.85 g (61.89%) (Figure 20). The extraction took approximately 20 minutes at 94^{0}C. In this case, the first drop was recovered at 82^{0}C.

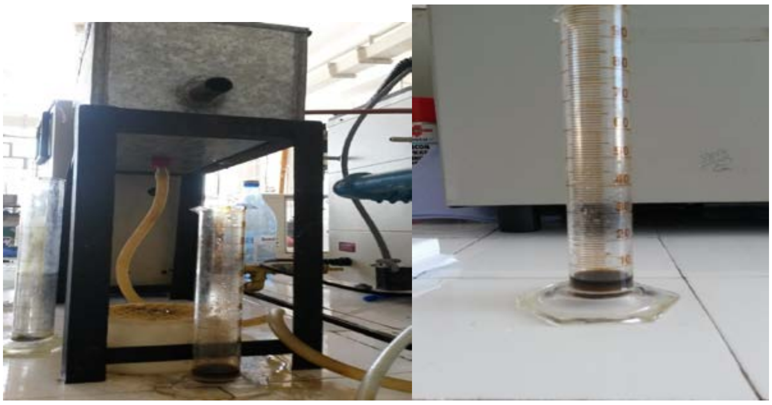

Fig. 20. The recovery of petroleum product from the mixture sunflower seed cake and Rebco crude oil

In most cases, after sorption, the crude oil-saturated sorbent material is shipped back to the bio power plant and burned (incinerated). Burning is not an optimal solution.

Through this experiment, it was demonstrated that it can be recovered by extraction more than 50% of the petroleum products from soaked adsorbents. The recovered petroleum products (light petroleum) can be mixed with other petroleum products (oil residues, heavy crude oil) and further processed.

3.1.4. Test for buoyancy

In this experiment, we studied if the adsorbent settles on the bottom of the vessel or not. In static conditions, the sorbents (peat moss, sunflower seed cake, sunflower hulls and polypropylene) as received, are placed in a beaker filled with 200 mL deep layer of demineralized water. After 15 minutes and after 24 hours, observations are done and the sorbent is removed from water (Figures 21-23).

The observations carried out on the analyzed samples showed very good behaviour of polypropylene sorbents, sunflower hulls and peat moss. The sunflower seed cake type 1 also has settled on the bottom of the vessel engaging the oil particles.

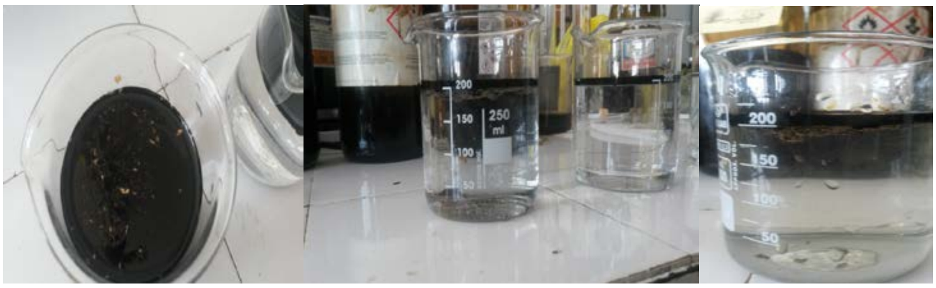

Fig. 21. The behaviour of sunflower seed cake in water and Rebco crude oil

Fig. 22. Sunflower seed cake type 1 fails the test after 15 minutes

Fig. 23. The behaviour of sunflower hulls in water and light vacuum oil

3.1.5. Test of sorption from a solid surface

The four adsorbents were tested for sorption from a solid surface. The sorption capacities from a solid surface were measured by adding a known amount of crude oil (cca. 3g) to the surface of a piece of stone and applying the sorbents (cca. 4g) on top of the stone. The sorbents were let in contact with the polluted stone surfaces over night and the sorbent and stones were weighted [9].

There was no significant difference in the sorbents ability to sorb crude oil from the surface of stone. The results are given in Table 7.

Table 7

The approximately removal efficiency with the sorbents tested from the surface of stone

Natural adsorbent	Rebco crude oil adsorbed (%)	Waxy crude oil adsorbed (%)	Asphalt crude oil adsorbed (%)	Vacuum light oil adsorbed (%)
Sunflower seed cake	93	94	94	95
Sunflower hulls	89	84	82	80
Peat moss	99	98	98	99
Polypropylene	99	99	99	98

4. Conclusions

This study has confirmed the following conclusions:

- Agricultural sorbents (like sunflower hulls, sunflower seed cake, peat moss) are cheap, efficient, environmentally friendly and are generally disposed as wastes;
- The efficiency is dependent on sorption capacity, density, retention, wettability and recyclability;
- Peat moss has been widely the most efficient natural sorbent used in oil spills; also, polypropylene is very efficient synthetic sorbent but it is not biodegradable;
- Sunflower hulls, peat moss and polypropylene float on the water surface for a very long period of time but the buoyancy tests of sunflower seed cake type 1 indicated the inability to be used in any water oil-spill conditions;
- From the preliminary studies of this natural sorbents, it can be concluded that peat moss and sunflower hulls can be used in oil spills and sunflower seed cake type 1 in shoreline and beaches;
- The recovered petroleum products from the mixture of sunflower seed cake and Rebco crude oil can be used as high-energy fuel; however, the need for further research to investigate others characteristics is essential;
- The sorption capacity of the sorbents followed the general trends: polypropylene > peat moss > sunflower seed cake > sunflower hulls;
- Natural sorbents don’t eliminate toxic emissions into the environment and don’t have a negative impact on living creatures;
- Heavy crude oils are retained within the peat, sunflower seed cake and sunflower hulls pores by adsorption, this sorbents acting as a sponge that collects the product by capillary phenomena;
- Sunflower seed cake and sunflower hulls could be new biodegradable sorbents with average sorption properties.

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MODEL-BASED OPTIMIZATION OF BIOCHEMICAL REACTORS INCLUDING INTERCONNECTED COMPLEX ENZYMATIC PROCESSES

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Abstract

Due to the overwhelming contribution of the enzyme cost (including its immobilization/stabilization) in the final product selling cost for most of the industrial biosyntheses, the study is focused on applying a modular screening procedure for selecting and optimizing the operation of enzymatic reactors for a completely specified enzymatic process. The case study refers to the complex oxidation of D-glucose (DG) to 2-keto-D-glucose (kDG), the optimal reactor policy corresponding to the minimum amount of required P2Ox (pyranose 2-oxidase) and catalase that ensures an imposed reaction conversion and reactor productivity under various technological constraints.

Key words: enzymatic process, model-based optimization, D-glucose oxidation

1. Introduction

When developing a new/improved enzymatic process at an industrial scale, one crucial engineering problem concerns determination of the optimal design and operation alternative that extremizes a performance index, called ‘cost function’, in financial or engineering units [3,4]. The optimal operating policy depends on the enzymatic process characteristics, and reactor type. Solutions are not easy to find, even if a process model is available, due to the presence of multiple (often contrary) objectives, technological constraints, and an important degree of uncertainty in model, parameters, constraints, raw-material and enzyme quality [5]. For multi-enzyme systems, the reactor choice and optimization is even more difficult due to complex interactions among enzymatic reactions, beside differences in enzymes optimal activity domains of temperature and pH.

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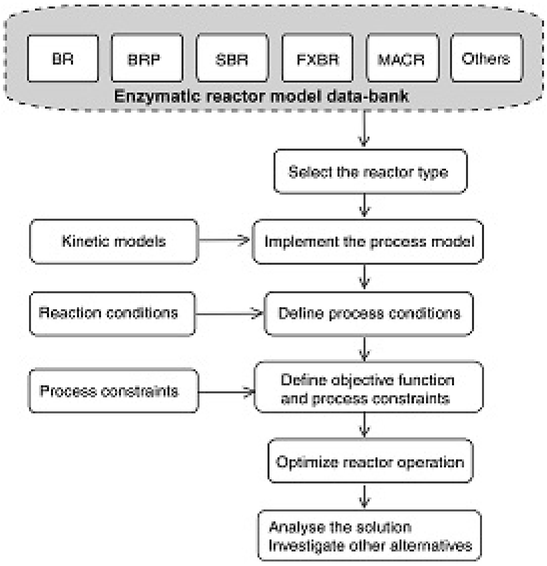


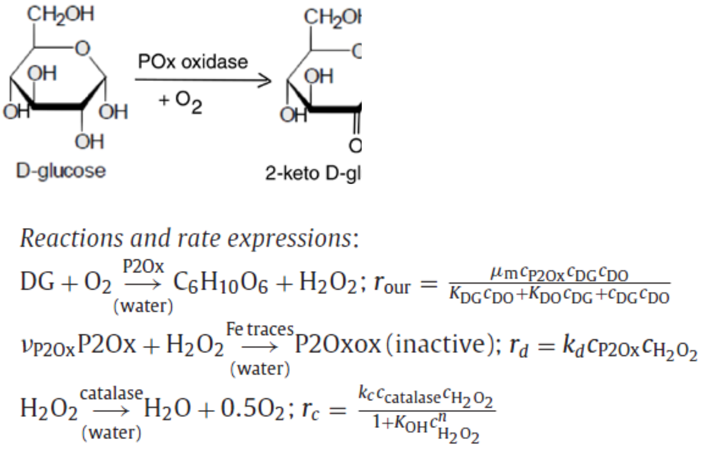
Fig. 1. Modular platform for enzymatic reactor selection and optimization (adapted from Maria [1])

Recently, Maria [1] developed a modular simulation platform able to evaluate, based on ideal models (Fig. 1), the optimal operation policies of single-enzyme / single-objective reactors including batch (BR), batch with intermittent addition of enzyme (BRP), semi-batch with enzyme optimal feeding policy (SBR), fixed-bed (FXBR) or mechanically agitated continuous reactors (MACR) with immobilized enzyme on suspended porous supports (of small size particles). Maria & Crișan [6] extended application of such a systematic strategy by screening among optimized reactors for the case of DG oxidation to kDG using P2Ox and catalase in the temperature range of 25-30°C. The present paper aims at extending optimization of this bi-enzymatic process by checking different reactor capacities with considering the enzyme inherent biodegradation together with its complex chemical inactivation.

2. Experimental

The optimal design and operation alternative for the chosen bi-enzymatic system of high complexity is determined using a modular simulation platform developed by Maria [1]. The platform is able to evaluate, based on ideal models and by using a random search MMA optimization procedure [2], the optimal operating policies using two enzymes coupled with the best reactor type/ running condition alternative selection.

Process description. The approached DG oxidation to kDG is the first step of the Cetus process for DG conversion to D-fructose of high purity [7] (Fig. 2). The effect of catalase addition is as follows: i) increase P2Ox activity by H_2O_2 decomposition, and ii) decrease the P2Ox deactivation rate [8].



Reactions and rate expressions:

$$DG + O_2 \xrightarrow[\text{(water)}]{\text{P2Ox}} C_6H_{10}O_6 + H_2O_2;\ r_{our} = \frac{\mu_m c_{P2Ox} c_{DG} c_{DO}}{K_{DG} c_{DO} + K_{DO} c_{DG} + c_{DG} c_{DO}}$$

$$\nu_{P2Ox} P2Ox + H_2O_2 \xrightarrow[\text{(water)}]{\text{Fe traces}} P2Oxox\,(\text{inactive});\ r_d = k_d c_{P2Ox} c_{H_2O_2}$$

$$H_2O_2 \xrightarrow[\text{(water)}]{\text{catalase}} H_2O + 0.5O_2;\ r_c = \frac{k_c c_{catalase} c_{H_2O_2}}{1 + K_{OH} c^n_{H_2O_2}}$$

Fig. 2. Reaction scheme and kinetic model for the enzymatic oxidation of DG (adapted from Maria [7])

The reaction occurs at 25-30°C and pH=6-7 using recombinant P2Ox (EC 1.1.3.10) with more than 99% DG conversion (xDG) and selectivity leading to kDG product of high purity and free of allergenic compounds. The process is still very costly due to the expensive and fast deactivating P2Ox due to the resulted H_2O_2. To prolong P2Ox life, catalase (EC 1.11.16, from bovine liver) has been added in large [catalase]/[P2Ox] ratios (up to 300/1-1000/1 U/U) to decompose H_2O_2 [7, 9]. For the investigated temperature of 30°C (optimal for P2Ox activity), Maria et al. [7] proposed a kinetic model accounting for three main reactions (Fig. 2).

3. Results and discussions

Derivation of optimal operating policies for the approached enzymatic reactors is made for the BR and MACR cases. From the mathematical point of view, the single objective (BR case), or two-objectives (MACR case) reactor optimization problem consists in finding the manipulated variable (control) vector $\boldsymbol{u}$ of fed P2Ox to get an imposed DG conversion ($x_{f,imp}$= 0.99), an imposed final batch (t_f =10 hr, BR), or residence time (V_L/f_o = 10 hr, MACR), and given reactor volume (V_L = 10m^3), such that:

$$\boldsymbol{u} = \arg\mathrm{Min}\,\Omega;\quad \Omega = \{[E]^{MACR}_{\sup,o}; [E]^{BR}_{inj}; -t^{MACR}_{onstream}\},\ \text{with: } \boldsymbol{u}^{BRP} = [V_{inj,1},..,V_{inj,Ninj},[E]^{BRP}_{inj}],\ \boldsymbol{u}^{MACR} = [f_1,.., f_N, [E]^{MACR}_{\sup,o}] \tag{1}$$

subject to: $|x_f - x_{f,imp}| \le$ toll(0.001); $d[\boldsymbol{c},V]/dt = \boldsymbol{H}(\boldsymbol{c},\boldsymbol{f},\boldsymbol{\phi},V,t)$,(dynamic process model); $[\boldsymbol{c},V](t_o) = [\boldsymbol{c}_o,V_o]$, (initial conditions; $[DG]_o$=0.25M, [DO*]=0.2484mM);

$[\boldsymbol{c}, V_{inj,u}, f_u] \geq 0$; $\{[E]_{sup,o}, [E]_{inj}, [E]_{in}\} \in [[E]_{min}, [E]_{max}]$; [kDG] ≥1M (MACR); $f_u^{MACR} \in$ [0.5,5] m^3/h $\wedge$ $f_u^{MACR} \geq 0.9\, f_o$; maximum dilution of $\sum_u V_{inj,u} = 0.1V_o$ (BRP); $t_{onstream}^{MACR} \geq 2$ days; minimum capacity of 360 t DG/yr.

The used notations are: $\boldsymbol{c}$ is the species concentration vector, $V_{inj,u}$ are the injected volumes of enzyme (E); $f_u(t)$ are the feed flow rates of inlet substrate DG (MACR) or enzyme E solution, over $u = 1,\ldots,N_{div}$ equal time-intervals (MACR)(for MACR an adopted small Δt = 10 min is used to check the $f_u(t)$ constancy); $\boldsymbol{\phi}$ is the model parameter vector, DO is the dissolved oxygen; the indices are: 'o'=initial, 'in'=inlet, 'sup'= support, 'inj'= injected.

Optimization was performed by using a random search MMA optimization procedure [2], by determining the minimum amount of required net P2Ox and catalase (BR case) and also ensuring a longer running batch for high reactor productivity (MACR case).

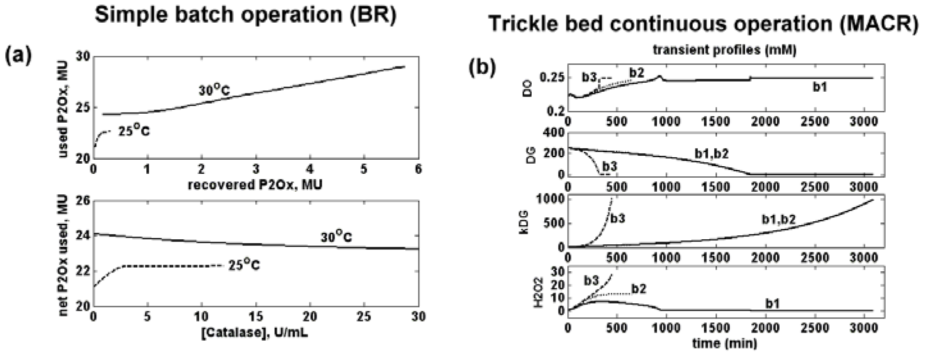


Fig. 3. (a) Total and net consumption of P2Ox *in the BR*. The operating temperature is 25°C (• • • lines), and 30°C (—lines). The setpoint at 25°C corresponds to $[P2Ox]_{inj}$ = 22.5 U mL^{-1}, [catalase] = 12 U mL^{-1}, while setpoint at 30°C corresponds to $[P2Ox]_{inj}$ = 29 U mL^{-1}, [catalase] = 30 U mL^{-1}; (b) *MACR operation alternative*: The key species concentration dynamics for a variable feeding policy with DG solution. The operating temperature is 30°C, $[DG]_{in}$ = 0.25 M, pH = 6.5. Reactor operation is stopped when the initial feeding flow rate is diminished with more than 10% (b2 lines), and/or when [E] < 0.1 $[E]_0$ (b2 lines), and/or when [kDG] > 1 M (b1 and b3 lines). The setpoints are (f_o = 0.67 m^3 h^{-1}): 30°C, $[P2Ox]_0$ = 1 U g^{-1} (0.258 U/mL-lq.), [catalase] = 100 U g^{-1} (25.8 U/mL-lq.), with: (b1 — lines): d_p = 1 mm; f_o = 0.67 m^3 h^{-1}, (b2 • • • • • lines): d_p = 2 mm; f_o = 0.67 m^3 h^{-1}, (b3 - - - lines): d_p = 1 mm; f_o = 6.70 m^3 h^{-1} (adapted after Maria and Crișan [6])

A comparison between BR and MACR (Fig. 3) shows that the MACR operation alternative is the most efficient, by consuming 10 times less enzyme than BR, even if the recovering possibilities are modest (only 15-20% of initial P2Ox comparatively to 35-80% for BR)[6]. For a catalase/P2Ox ratio of 100 U U^{-1} ratio, MACR might continuously operate up to one week at high conversion, being stopped after 3100 min. of operation due to the accumulation of a high level of kDG product. The enzyme P2Ox consumption is of 0.008MU per tonne of converted DG that is much lower than 0.08-0.160 MU per tonne DG for BR case.

4. Conclusions

If the process kinetics and enzyme deactivation characteristics are specified, a systematic engineering approach using a modular reactor simulation platform can offer a large number of possibilities in assessing the optimal selection and operating alternatives among various enzymatic reactors. From a larger perspective, a decision on choosing a suitable bioreactor feeding policy that achieves a satisfactory productivity is more complex, depending not only on raw materials, product and batch costs, but also on the production capacity and investment costs, optimal operating solution implementation costs, control system cost and costs of lost batches, all being connected to the market requirements.

Acknowledgements

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INTEGRATED PROCESSES FOR BIO-ETBE SYNTHESIS

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Abstract
The environmental legislations have facilitated the need to introduce on the market gasoline additives that have the purpose of increasing octane number as well as decreasing gaseous emissions. The purpose of this study is to select a feasible ETBE synthesis process and explore it using modeling and simulation techniques in order to test the process for bio-ETBE synthesis using bio-ethanol and C4 fractions from Fluid Catalytic Cracking unit as feedstock. The study consists of a literature review and a simulation of the selected bio-ETBE production process using Aspen HYSYS® v.8.6.

Key words: bio-ETBE synthesis, bio-ethanol synthesis, process simulation

1. Introduction

Ethyl tert-butyl ether (ETBE) is used as gasoline additive in order to improve performance by increasing the octane number and decreasing the CO emissions. Gasoline has poor combustion characteristics when used in internal combustion engines, therefore the additives are needed to avoid gasoline pre-ignition.

ETBE has the advantages of having low Reid vapor pressure (RVP), low solubility in water and it can be produced from renewable resources (Ancilloti, 1998).

Sugars present in this biomass are fermented to produce bio-ethanol used as feedstock for bio-ETBE production along with and C4 fractions from Fluid Catalytic Cracking unit (FCC).

On an industrial scale, the conventional ETBE synthesis process consists basically of reaction section and separation section, with recycle loop. Typical industrial processes are based on liquid phase reactions catalyzed by acidic ion-exchange resins. The separation section includes two fractionation column and one L-L extraction column due to the formation of C4-ethanol azeotrope.

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Mostly, bio-ethanol is produced from alcoholic fermentation of $C_6H_{12}O_6$ from molasses in presence of yeast (Ruhul, 2013). In this paper is considered the process presented in Fig. 1.

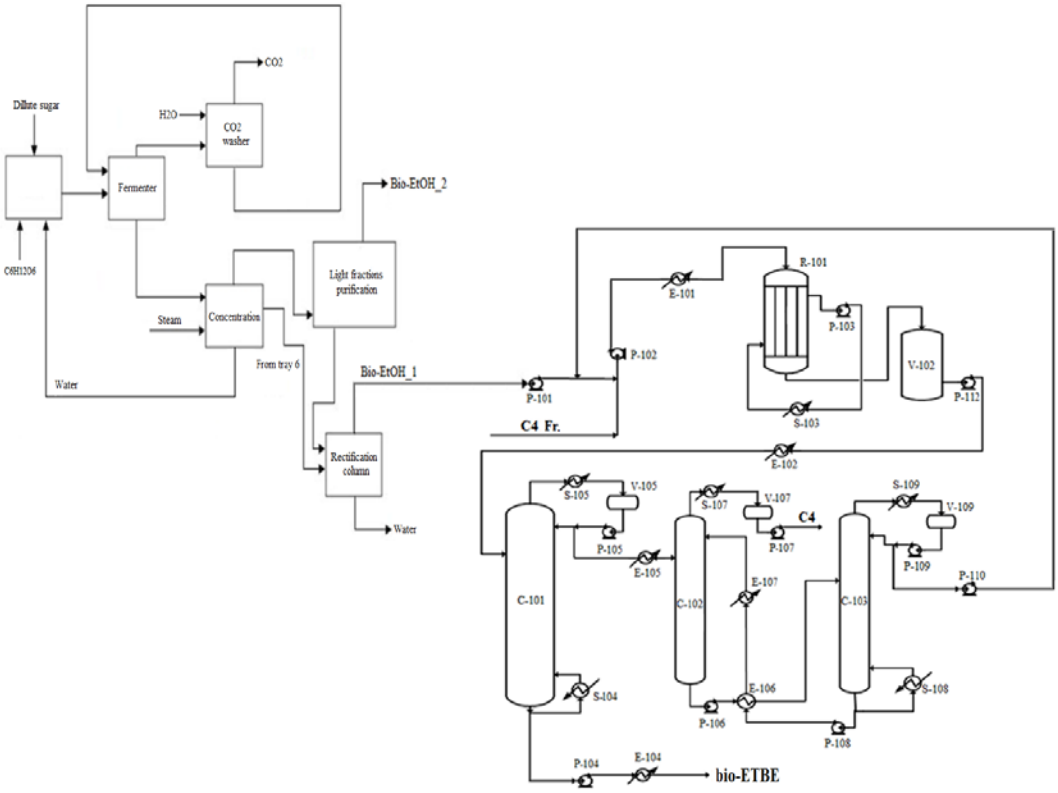


Fig. 1. Process flow diagram of bio-ETBE synthesis process

2. Methodology

2.1. Aspen HYSYS Process Simulation

Aspen HYSYS v.8.6. is used as process simulator. Selected fluid packages are UNIQUAC, Wilson and NRTL. UNIQUAC and Wilson were selected due to the presence of bio-ethanol in the liquid phase which determines a non-ideal behavior of the mixture. The NRTL model fits best to the equilibrium of fermentation reaction because the components involved in the process have characteristics of polarity and electrolytes (Carlson, 1996).

The feedstock, also presented in Table 1, is $C_6H_{12}O_6$ from molasses and C4 fractions from Fluid Catalytic Cracking unit.

Table 1.

Molar composition of the industrial load of bio-ETBE synthesis

Crt.	**Stream name**	**Mass flow, kg/h**	**Concentration, mol.%**							
			i-C_2H_4	**i-C_2H_6**	**1-C_2H_4**	**ETBE**	**EtOH**	**H_2O**	**$C_6H_{12}O_6$**	**CO_2**
In	$C_6H_{12}O_6$	7269	0	0	0	0	0	0	100	0
	C4 Fr.	9900	19.4	5.8	22.4	0	0	0	0	0
	Water	5885	0	0	0	0	0	100	0	0
Out	CO_2	2830	0	0	0	0	0.03	0	0	99.7
	Lights	57	0	0	0	0	0	0,1	0	99.9
	Bio-EtOH_2	153	0	0	0	0	100	0	0	0
	Bio-ETBE	3052	0.83	2.35	6.12	85.4	4.8	0,5	0	0
	C4	8440	2.7	23.7	70.8	2.2	0	0,6	0	0
	Water	8582	0	0	0	0	0	100	0	0

Reactions

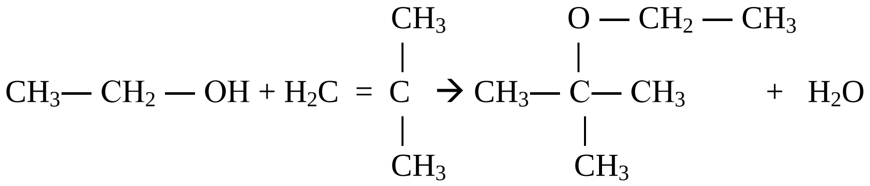
Two reactions occur in the formation of bio-ethanol from molasses, one is for fermentation (1) and another is for conversion of fructose to bio-ethanol (2). Catalyst of fermentation reaction is invertase enzyme from yeast and catalyst of bio-ethanol conversion reaction is zymase. In this study only reaction (2) was considered and modeled as conversion reaction.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \qquad \textbf{(1)}$$

(sucrose) (glucose)

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 \qquad \textbf{(2)}$$

(glucose) (bio-ethanol)



$$CH_3—CH_2—OH + H_2C=C(CH_3)_2 \rightarrow CH_3—C(CH_3)(O—CH_2—CH_3)—CH_3 + H_2O \qquad \textbf{(3)}$$

(bio-ethanol) (i-butene) (bio-ETBE)

Process Thermodynamics

The synthesis of bio-ETBE from the reaction of bio-ethanol with isobutene (3) is an exothermic reaction of equilibrium. In order to increase the conversion of isobutene, the reaction system requires operating at low temperatures and with excess of bio-ethanol to displace the equilibrium towards the products. Fig.2. presents the isobutene conversion as function of temperature (Sundmacher, 1995).

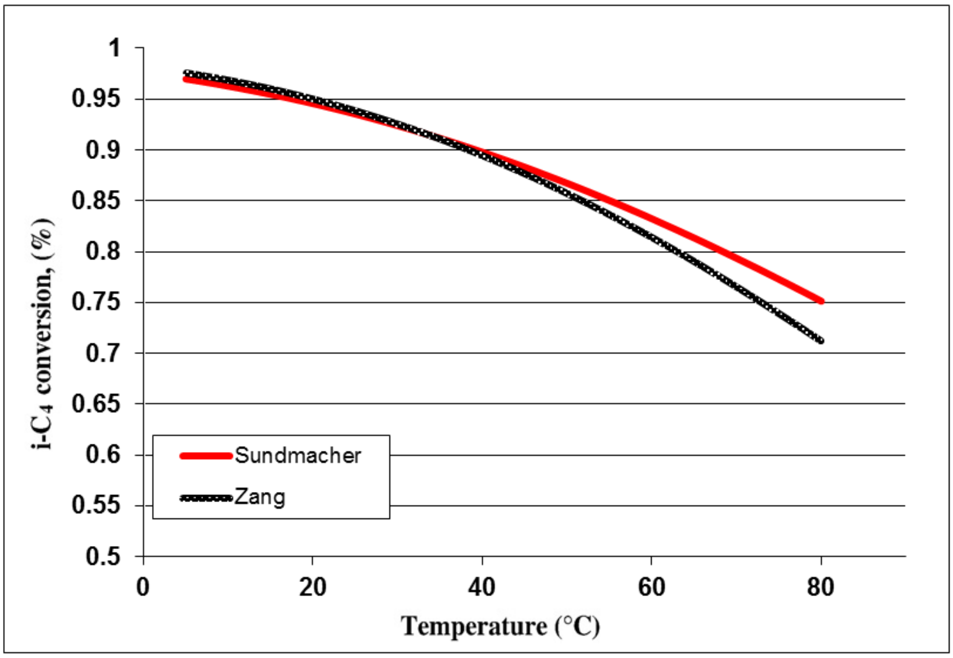


Fig. 2. Process flow diagram of bio-ETBE synthesis process

Process description

Dissolved sugar from molasses is diluted by mixing with water and before feeding the fermenter is added the yeast which provides the enzymes (invertase and zymase). First sucrose is degraded through hydrolysis in the presence of invertase to glucose and fructose. Glucose and fructose is converted into bio-ethanol and carbon-dioxide by zymase. CO_2 gas leaving the fermenter carries away some bio-ethanol with it (Ruhul, 2013).

The gaseous stream is sent to an absorption column, referred to as CO_2 Washer, where the bio-ethanol is absorbed by wash water. The vapors leaving the absorber contains very low amount of bio-ethanol and is vented in atmosphere. The liquid stream leaving the column is recycled to the fermenter.

The liquid stream leaving the fermenter is a very dilute bio-ethanol solution which also contains some sucrose, glucose and fructose. This stream is sent to a stripping column referred to as Concentration Tower. The stripping gas used in this column is superheated steam at atmospheric pressure. The Liquid Stream from the bottom of the Concentration Tower contains water which is recycled into the fermenter. A side stream from the 6 theoretical stage of this column is sent to a distillation column referred as to the Rectification Tower. The gaseous stream emerging from the top of the Concentration Tower is sent to a refluxed absorber column with partial condenser referred to as Light Purification Tower.

The gas stream leaving the condenser of the Light Purification Tower has low bio-ethanol concentration and low flow rate. The rest of CO_2 gas which was not removed by the CO_2 Washer is vented to atmosphere by this stream. The liquid stream leaving the bottom of Light Purification Tower which is a dilute bio-ethanol solution with no other component is sent to the Rectification Tower.

The Rectification Tower has two feed streams, one from Concentration Tower and the other one from Light Purification Tower. The condensate from this unit is light bio-ethanol with 74.23% concentration. Concentrated bio-ethanol with 88.14% content is sent out from the 2nd theoretical stage of the Rectification Tower as feedstock for the bio-ETBE synthesis process.

In the bio-ETBE synthesis process, bio-ethanol with C4 fraction go through the following steps: etherification reaction, de-butanization of reaction mixture, bio-ethanol extraction, bio-ethanol recovery from the extract.

The synthesis of bio-ETBE, is carried out by addition of ethanol to isobutene from the C4 hydrocarbon fraction in the presence of AMBERLYST catalyst, followed by the concentration of the product (bio-ETBE) by fractional distillation (Halim, 2004).

From the reaction stage, the resulting product is sent to the debutanizer column, where the vapor from the top of the column are condensed and the fraction C4 - ethanol is collected in the reflux vessel, from where it is pumped to the extraction column (washing with water) to remove the ethanol fraction.

The product from the bottom of the wash column is sent to ethanol recovery column, where ethanol is purified by fractionation. The ethanol recovered from the distillate of the column is recycled to the reaction step.

2.2. Environmental Impact

Environmental impact is evaluated with Waste Reduction Algorithm software v.1.0.15.0. The method is based on a potential environmental impact (PEI) units produced for fuel gas, when the products are bio-ETBE, C4 and CO_2 streams.

2.3. Economical Evaluation

Economical Evaluation was performed with Capcost program in order to estimate the capital investments cost of the bio-ETBE synthesis process.

3. Results and discussions

3.1. Aspen HYSYS Process Simulation

Simulation work is performed in order to test the possibility of using bio-ethanol and C4 fractions from Fluid Catalytic Cracking unit as feedstock for bio-ETBE synthesis process in the existing industrial process of ETBE.

In Fig. 3 is presented the process flow diagram implemented in Aspen HYSYS simulator.

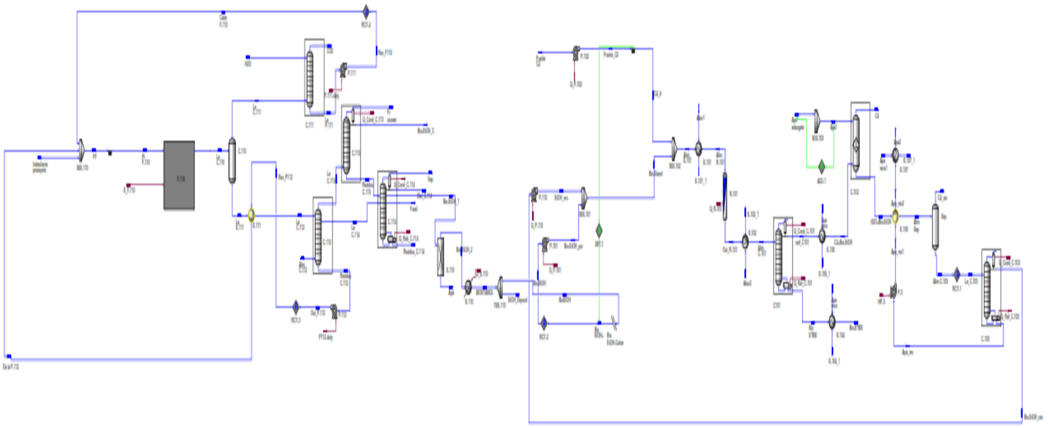


Fig. 3. Process flow diagram of bio-ETBE production from bio-ethanol and isobutene

In Table 2 is presented the mass balance obtained from the simulation of bio-ETBE synthesis.

Table 2.

Material balance of bio-ETBE synthesis process

Feed (kg/h)	
$C_6H_{12}O_6$	7269
Water	5885
C4 Fr.	9900
Products (kg/h)	
CO_2	2830
Lights	54
Fus.	3
Bio-EtOH_2	153
Water	8582
C4	8380
Bio-ETBE	3052
Total:	**23054 kg/h**

3.2. Environmental Impact

Fig. 4. presents PEI/kg for both ETBE and bio-ETBE synthesis processes. The processes generate large PEI units, because C4 fractions have important environmental impact.

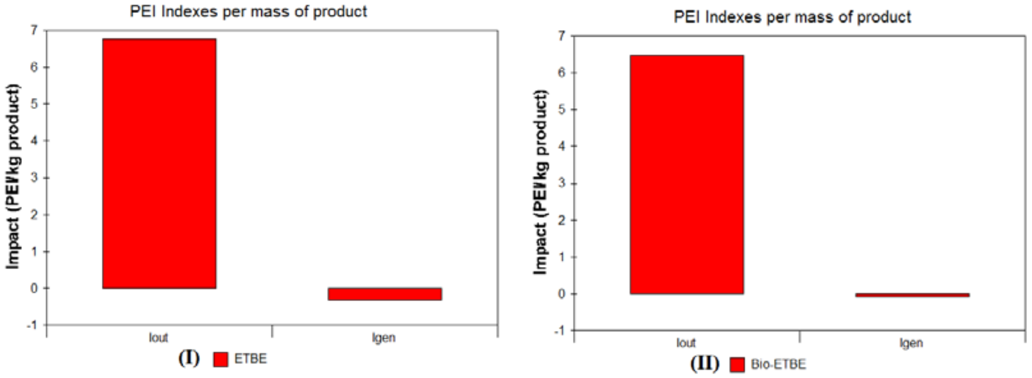


Fig. 4. Environmental impact for ETBE synthesis process (I) and bio-ETBE synthesis process (II)

3.3. Economical Evaluation

Table 3. presents the capital investment cost for ETBE and bio-ETBE production processes. For bio-ETBE production process the value of the investment cost was 64 mio. € with return on investment of 68 %.

Table 3.

Capital investment cost for ETBE and bio-ETBE synthesis processes

Synthesis process	Stream	Mass flow, kg/h	Quantity, t/an	Price, €/t	Cost, €/t/an
ETBE **Bio-ETBE**	Cooling water	3995	31960	0,9	28764
	LP Steam	1700	13600	30	408000
	i-C4 Fr.	9900	79200	570	45144000
ETBE	Ethanol	1600	12800	500	6400000
		MWh	**MWh/an**	**Euro/MWh**	**Cost, €/MWh/an**
	El. Energy	2,84	22720	25	568000
	Total Cost				**52,5 mio. €**
Bio-ETBE	Molasses	2715	21720	750	16290000
		MWh	**MWh/an**	**Euro/MWh**	**Cost, €/MWh/an**
	El. Energy	10,9	87200	25	2180000
	Total Cost				**64 mio. €**

4. Conclusions

Bio-ETBE synthesis process produces lower carbon dioxide emissions and, if obtained from renewable resource, reduces the dependence on oil and increases the nation’s energy independence. Simulation results indicate that is posible to produce bio-ETBE in the conventional process of ETBE synthesis, with a higher investment cost, but lower environmental impact.

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LIFE CYCLE ANALYSIS (LCA) OF VARIOUS ALTERNATIVES FOR BENZENE PRODUCTION

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Abstract
This study compares the life cycle impacts of various alternative for benzene production. The environmental life cycle impact is evaluated within the Life Cycle Analysis (LCA) methodological framework. Three cases have been investigated: benzene productions from toluene dealkilation, benzene production from reformate, benzene production from pyrolysis fuel. The system boundaries considered in the LCA study include (i) benzene production process using different raw materials, (ii) upstream processes such as steam production from natural gas and (iii) downstream processes such as benzene transportation to another chemical plant. Several environmental impact categories were calculated and compared. The most significant environmental impact categories are Global Warming Potential (GWP), Acidification Potential (AP), Freshwater Aquatic Ecotoxicity Potential (FATEP), Human Toxicity Potential (HTP), Marine Aquatic Ecotoxicity Potential (MAETP). The best value for GWP, 828.86 kg CO_2*-Equiv./ton and for AP 2.97 Kg SO2-Equiv./ton was obtained when benzene is produced from reformate. The best values for the impact categories related to lethal concentration (FAETP, HTP, MAETP) is obtained when benzene is obtained from pyrolysis.*

Key words: Benzene production, Life Cycle Assessment (LCA)

1. Introduction

The petrochemical industry is one of the most important economic forces on a global or local scale, and it provides materials for many industries its products being used in all life sectors. Benzene is a major product of the petrochemical industry being considered the most important and versatile aromatic compound [1]. Primary derivatives of benzene that have large volume commercial use are ethylbenzene, cumene, cyclohexane, and nitrobenzene. Hundreds of benzene derivatives are formed by the replacement of one or more of its hydrogen atoms with other elements, groups, or side chains. These intermediate chemical products are in turn converted to other chemicals, plastics, resins, elastomers, fibers, or surfactants. Figure 1 provides an overview of the major benzene derivatives and the final consumer products that are made from them [2].

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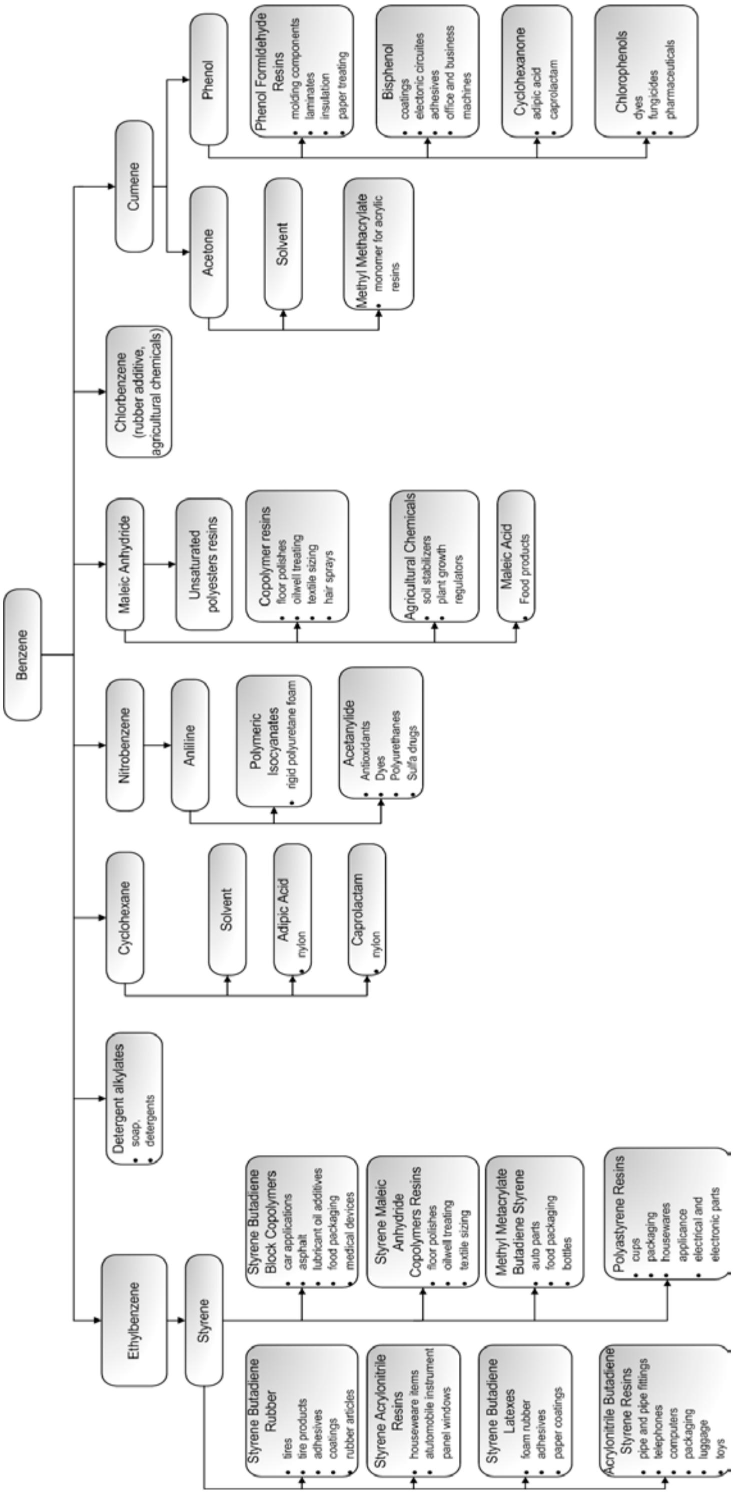

Fig. 1. Majour benzene end uses

Benzene is produced commercially by five processes: 1) destructive distillation of coal (by-product of steel mill coking process); 2) catalytic reforming of petroleum - based naphtha; 3) recovery from pyrolysis gasoline (pygas), a co-product stream from the steam cracking process used to manufacture ethylene (the ethylene co-product process); 4) hydrodealkylation of toluene (HDA process); and 5) toluene disproportionation process (TDP). The first three processes involve the production of benzene from a C6 hydrocarbon stream by solvent extraction. In the latter two processes, the benzene product is separated from the reactants and co-products by distillation. Benzene production directly from toluene accounts for approximately 25% of the total benzene produced.

In this context, being so much used all over the world, the environmental impact of such a process should be quantified. This approach is important for the petrochemical industry in order to reduce its environmental impact.

2. Process description

The toluene hydrodealkylation process schema is presented in Figure 2 [3].

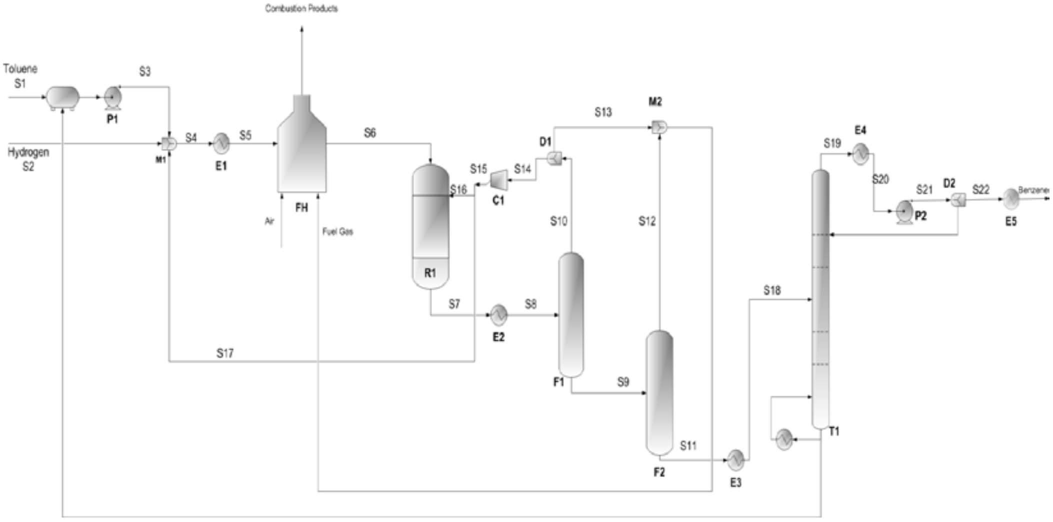

Fig. 2. Benzene production from toluene hydrodealkylation

Fresh toluene stream S1 is mixed with the recycled toluene and fresh hydrogen S2. Before being sent to the reactor, the mixed stream is preheated, in the heat exchanger E1, up to 225˚C, using medium pressure steam. This temperature is not sufficient to initiate the reaction; consequently the mixed reagents stream is heated using a fired heater. The fuel gas resulted in the process is burned in the fired heater in order to generate the requested heat. The temperature is raised up to 600˚C. The toluene dealkylation takes place in the reactor according to the following chemical reaction:

$C_7H_8 + H_2 = C_6H_6 + CH_4$

The reactor is packed with catalyst and typically the reaction reaches a conversion of 90%. The reaction is highly exothermic and the operating conditions are 500˚C - 660˚C, and 20 - 60 bar. The reaction products are sent to the separation section. Before this, the reaction products are colled down using E2 heat exchanger. In the first instance the gases, more exactly the methane formed in the reaction and the unreacted hydrogen, are separated in two phase separators (the first separator F1 is working at high pressure e.g. 24 bar, the second one F2 is working at low pressure e.g. 2.9 bar). The gaseous stream coming from the separators are mixed and they represent the fuel gas burned in the fired heater FH. The liquid phase, stream S11, is sent to the distillation column T1 in order to separate the process product, more exactly benzene from the unreacted toluene. After the separation the benzene product is sent to storage while the unreacted toluene is recycled back to the reaction section. Many facilities that produce benzene from petroleum sources also have the ability to produce benzene from toluene via HDA. The HDA process is reported to be economically feasible when low-cost hydrogen is available [4].

3. Process modelling and simulation

ChemCAD process simulator has been used to simulate the above described process. The most important process input streams are reported in Table 1.

Table 1.

Input streams specifications for benzene production process

Stream name		**S1**	**S2**
Stream description			
Temperature	C	25	25
Pressure	bar	1.9	25.5
Rate	kmol/h	108.7	301
Component rate	kmol/h		
Hydrogen		0	286
Methane		0	15
Benzene		0	0
Toluene		108.7	0

The main assumptions used in the simulation are presented in Table 2.

Table 2.

Main design characteristics for benzene production process

Equipment/Unit	**Case 1**
Reactor	Catalyst packed bed 660˚C 25 bar
Pumps	Centrifugal/electrical Efficiency 75%
Compressor	Centrifugal/electrical Efficiency 75%
Cooling water temperature	20˚C
Heat Exchanger ΔTmin	10˚C
Fired heater	Duty 27040 MJ/h Fuel gas: aprox. 58% H_2 42% CH_4
Tower	42 sieves trays 99.5% efficiency

Table 3 contains the output streams of the process.

Table 3.

Output streams specifications for benzene production process

Stream name		**Benzene**	**Fuel gas**
Stream description			
Temperature	°C	38	38
Pressure	bar	2.3	2.5
Rate	kmol/h	105.6	304.2
Component rate	kmol/h		
Hydrogen		0	178
Methane		0	123
Benzene		105.2	2.85
Toluene		0.4	0.3

The thermodynamic system used for this simulation was the Soave-Redlich-Kwong (SRK), considering the chemical species involved and the operating pressure and temperature. The above described process was simulated using ChemCAD version 6.0.1 process simulator [5].

The following case studies have been considered and compared:

Case 1. Benzene production process from toluene dealkylation

Case 2. Benzene production process from pyrolysis;

Case 3. Benzene production process from reformate;

Case 4. Benzene production process from toluene dealkylation (GaBi database).

4. Life Cycle Analysis (LCA)

Life Cycle Assessment (LCA) is an environmental management tool that enables quantication of environmental burdens and their potential impacts over the whole life cycle of a product, process or activity. Although it has been used in some industrial sectors for about 35 years, LCA has received wider attention and methodological development only since the beginning of the 1990s when its relevance as an environmental management aid in both corporate and public decision making became more evident [6].

One of the most comprehensive definitions of LCA was given by the Society for Environmental Toxicology and Chemistry. LCA is defined as a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment; to assess the impact of those energy and material uses and releases to the environment; and to identify and evaluate opportunities to effect environmental improvements. LCA is generally accepted as an application of system analysis whose prime objective is to provide a picture of the interactions of an activity with the environment, thus serving as a tool for environmental management. As such, LCA has two main objectives. The first is to quantify and evaluate the environmental performance of a product or a process and so help decision makers choose among alternatives. Another objective of LCA is to provide a basis for assessing potential improvements in the environmental performance of the system. The latter can be of particular importance to engineers and environmental managers, because it can suggest ways to modify or design a system in order to decrease its overall environmental impacts [6].

In order to deal with the complexity of LCA, the International Standards Organization (ISO) established a methodological framework called ISO 14044 for performing a LCA study, which comprises four phases, including Goal and Scope, Life Cycle Inventory (LCI) analysis, Life Cycle Impact Assessment (LCIA) and Interpretation [7]. These steps are depicted in Figure 3 and detailed in the next part.

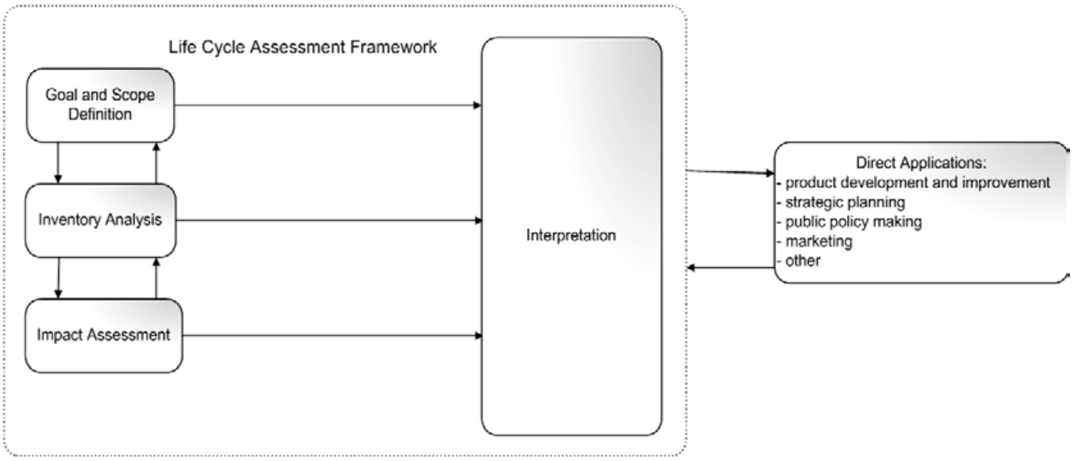

Fig. 3. Phases of LCA [7]

4.1 Goal and scope of the study, system boundaries, limitations and LCA main assumptions

The primary goal of this study is to quantify and analyse the total environmental aspects of benzene production from toluene dealkylation. For this aim, the following strategy is proposed: i) to provide a detailed assessment of each pathway step; ii) to provide a comparison of the environmental efficiency of the processes under study. The present LCA studies were conducted step by step, based on the energy and material consumption of each unit process which derived from the process simulator.

The scope of the study includes the definition of the following characteristics: function of the system, functional unit, geographical and temporal context, system boundaries, main assumptions and limitations. The functions of the systems considered in the present study are: the production of one ton of benzene. The plants are supposed to be located in Europe. The system boundaries include:

i) benzene production process;
ii) upstream processes such as: raw material for benzene production: toluene and hydrogen ; steam production using natural gas;
iii) downstream processes such as: benzene transport over a distance of 100 km to another chemical plant.

Figure 4 represents the system boundaries for the case under study.

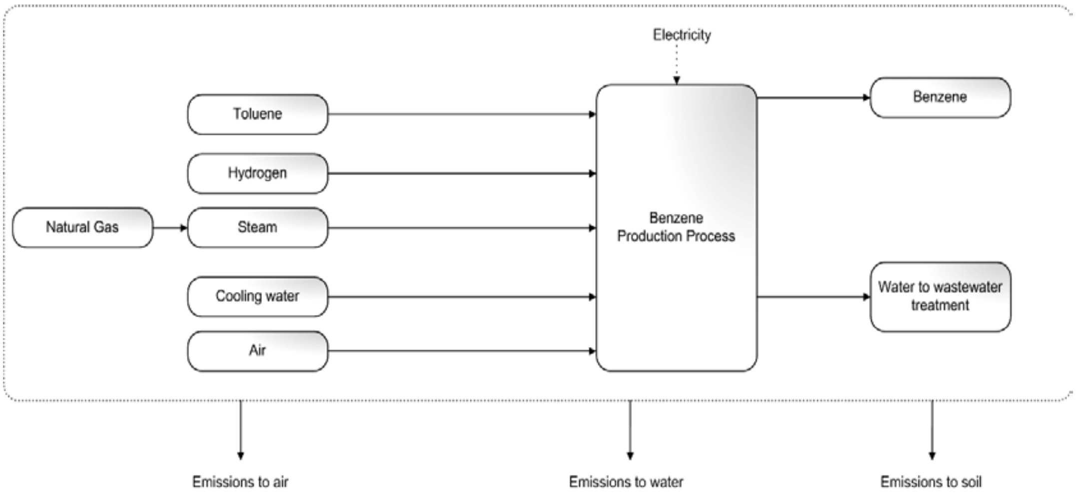

Fig. 4. System boundaries for LCA of benzene production process

A „cradle-to-gate” approach has been considered in the present study. „Cradle-to-gate„ is an assessment of a partial product life cycle from resource extraction (cradle) to the factory gate (i.e., before it is transported to the consumer). The use phase and disposal phase of the product are omitted in this case.

4.2 Life Cycle Inventory (LCI)

The LCI correspondent to each step was performed taken into account the quantities derived from the process simulator and the assumptions presented previously. The LCI table containing the inputs and outputs for **Case 1** is summarized below (see Table 4).

Table 4.

LCI for benzene production from toluene hydrodealkilation (**Case 1**).

INPUTS	Value	Units	OUTPUTS	Value	Units
Toluene	1218.86	kg/h	Benzee	1000	kg/h
Hydrogen	69.61	kg/h	Steam	717	kg/h
Air	6016.79	kg/h	Process water	50299.13	kg/h
Low pressure steam	59.69	kg/h	Carbon dioxide	764	kg/h
High pressure steam	657.16	kg/h	Water vapour	952.8	kg/h
Cooling water	50299.13	kg/h	Nitrogen	4765.07	kg/h

4.3 Impact Assessment

Impact assessment was carried out in order to identify the environmental impacts that arise from the LCI. The LCA software GaBi version 6.0 [8] was used to evaluate the environmental impacts of inventory aspects and to create product assemblies and life cycles for the case study.

The GaBi schema corresponding to **Case 1** is presented in Figure 5.

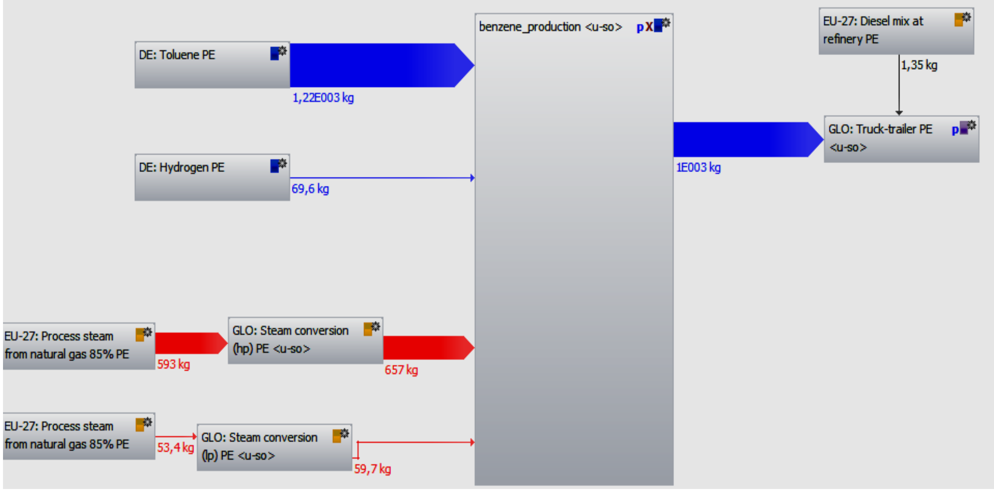

Fig. 5. GaBi schema for benzene production process using steam from natural gas

The CML 2001 method assessment, developed by Center of Environmental Science of Leiden University, was considered in the present study. The description of the environmental indicators considered in CML 2001 method is presented in Table 5.

Table 5.

Life Cycle Impact Categories [9]

Impact category	**Definition**	**Relevant LCI data**	**Common characterization factor**
Global Warming Potential (GWP)	Refers to the impact of anthropogenic emissions which enhance the radiative forcing of the atmosphere, causing the temperature at the earth's surface to rise.	CO_2, NO_2, CH_4, chlorofluorocarbons CFCs,hydro-chlorofluorocarbons HCFCs, methyl bromide CH_3Br.	CO_2 equivalents
Acidification Potential (AP)	Refers to the acidifying pollutants' potential impacts on soil, groundwater, surface waters, biological organisms, ecosystems and materials.	Sulphur oxides SOx, nitrogen oxides NOx, HCl, HF, NH_3.	SO_2 equivalents
Ozone Depletion Potential (ODP)	Refers to the thinning of the stratospheric ozone layer due to anthropogenic emissions.	Chlorofluorocarbons CFCs, hydrochlorofluorocarbons HCFCs, halons, methyl bromide CH_3Br.	Trichlorofluoromethane CFC-11 equivalents

Impact category	Definition	Relevant LCI data	Common characterization factor
Abiotic Depletion Potential (ADP)	Refers to the depletion of natural resources (including energy resources) which are regarded as non-living.	Quantity of minerals used, quantity of fossil fuels used.	converts LCI data to a ratio of quantity of resource used versus quantity of resource left in reserve
Freshwater Aquatic Ecotoxicity Potential (FATEP)	Refers to the potential impacts of toxic substances on aquatic ecosystem.	Toxic chemicals with a reported lethal concentration to fish.	converts LC_{50} data to equivalent
Human Toxicity Potential (HTP)	Covers the potential impacts on human health of toxic substances present in the environment.	Total releases to air, water and soil.	converts LC_{50} data to equivalents
Photochemical -Oxidantion Potential (PCOP)	Refers to the formation of reactive chemical compounds, such as ozone, by the action of sunlight on certain primary air pollutants.	Non-methane hydrocarbon NMHC.	ethane C_2H_6 equivalents
Terrestrial Ecotoxicity Potential (TEP)	Refers to the potential impacts of toxic substances on terrestrial and sediment ecosystems.	Toxic chemicals with a reported lethal concentration to rodents..	converts LC_{50} data to equivalents

5. Results and discussions

Eleven environmental impact categories were evaluated. The values of the environmental impact categories for **Case 1 - 4** are reported in Table 6.

Table 6.

LCA results according to CML 2001

KPI	UNITS	Case 1	Case 2	Case 3	Case 4
GWP	kg CO_2-Equiv./to	2696.19	1549.29	828.86	1494
AP	kg SO_2-Equiv./to	4.4	3.45	2.97	4.04
EP	kg Phosphate-Equiv./to	0.27	0.26	0.17	0.25
ODP*10^9	kg R11-Equiv./to	7.51	7.35	3.39	6.16
ADPelements*10^4	kg Sb-Equiv./to	2.25	4.01	1.33	2.21
ADPfossil*10^4	MJ/to	7.69	6.03	4.96	6.82
FAETP	kg DCB-Equiv./to	28.82	22.61	23.25	28.48
HTP	kg DCB-Equiv./to	77.07	52.87	61.09	76.05
PCOP	kg Ethene-Equiv./to	0.59	0.48	0.38	0.56
TEP	kg DCB-Equiv./to	0.7	0.57	0.54	0.7
MAETP*10^{-4}	kg DCB-Equiv./to	7.03	5.36	5.58	7.12

There are large differences in terms of GWP between the four cases under study. The total GWP value for **Case 1** is 2696.19 kg CO_2-Equiv./ton. From this value 1013.39 kg CO_2-Equiv./ton comes from the toluene production process, 762.07 kg CO_2-Equiv./ton comes from benzene production process, 756.23 kg CO_2-Equiv./ton comes from hydrogen production and he rest, 146.53 kg CO_2-Equiv./ton comes from steam production. It is considered that toluene is produced from reformate, hydrogen is produced from natural gas steam reforming and the steam requested by the process is produced from natural gas. Comparing the four cases, in terms of GWP, it can be noticed that the GWP value in **Case 3** is lower, more than three times, than the GWP in **Case 1**.

Regarding AP, the best value is obtained in **Case 3** (2.97 kg SO_2-Equiv./ton). The highest value is also obtained when benzene is produced from toluene dealkylation (**Case 1** and **Case 4**) e.g. 4.4 and 4.04 kg SO_2-Equiv./ton. The contributions of various steps to the AP value, for **Case 1**, is as follows: 3.62 kg SO_2-Equiv./ton comes from toluene production process, 0.618 kg SO_2-Equiv./ton is due to the hydrogen production process, 0.128 kg SO_2-Equiv./ton are due to steam production from natural gas. Truck trailer transportation of the final product (benzene) to another chemical plant has a minor impact (e.g. 0.017 kg SO_2-Equiv./ton) on the AP value.

The EP impact category has close values for **Case 1, Case 2** and **Case 4** (e.g. 0.27, 0.26 and 0.25 kg Phosphate-Equiv./ton. Other impact categories such as ODP and ADP elements have low values in all four cases. ADP fossil has the lowest impact in **Case 3** when benzene is obtained from pyrolysis gasoline and separated either by azeotropic distillation or by extractive distillation.

The highest values of the four impact indicators linked to the lethal concentration LC_{50}, FAETP, HTP, TEP, MAETP are obtained also in **Case 1.** PCOP impact category has similar values for **Case 1** and **Case 4**. The best value for this impact category is obtained also in **Case 3**.

It can be noticed from the data previously presented that **Case 1** is not the most environmentally friendly option. The most important contributors to various impact categories are the raw materials (toluene and hydrogen) production processes. Toluene was produced from reformate, hydrogen was produced from natural gas steam reforming and the steam requested by the process is produced from natural gas. In order to improve the environmental performance of toluene dealkylation other cases have been furthermore investigated. The cases are:

Case 1. Toluene from reformate, hydrogen from steam reforming of natural gas;

Case 1'. Toluene from pyrolysis, hydrogen from steam reforming of natural gas;

Case 1''. Toluene from pyrolysis, hydrogen from steam reforming of heavy fuel oil.

The results of the environmental indicators are reported in Table 7:

Table 7.

LCA results according to CML 2001

KPI	UNITS	Case 1	Case 1’	Case 1’’
GWP	kg CO_2-Equiv./to	2696.19	3745.07	3984.35
AP	kg SO_2-Equiv./t	4.4	5.91	6.12
EP	kg Phosphate-Equiv./to	0.27	0.46	0.47
ODP*10^9	kg R11-Equiv./to	7.51	32.7	39.7
ADPelements*10^4	kg Sb-Equiv./to	2.25	5.75	5.85
ADPfossil*10^4	MJ/to	7.69	9.25	9.13
FAETP	kg DCB-Equiv./to	28.82	30	35.29
HTP	kg DCB-Equiv./to	77.07	79.77	95.33
PCOP	kg Ethene-Equiv./to	0.59	0.90	0.91
TEP	kg DCB-Equiv./to	0.7	0.89	2.04
MAETP*10^{-4}	kg DCB-Equiv./to	7.03	7.31	9.45

As it can be noticed from Table 7, the consideration of alternative routes for the raw materials (toluene and hydrogen) doesn’t improve the environmental performance of the process under study.

6. Conclusions

Benzene production process from toluene hydrodealkylation has been investigated in the present paper. The process was simulated using commercial process simulator software (ChemCAD) and, based on the material and energy balances derived from this, the environmental impact assessment was performed. The environmental impact assessment was performed using the Life Cycle Analysis (LCA) methodology using GaBi software. The environmental indicators of the base case (benzene production from toluene dealkilation) were compared to other cases where benzene is produced using other technologies (from pyrolysis or from reformate). The most significant environmental impact categories are Global Warming Potential (GWP), Acidification Potential (AP), Freshwater Aquatic Ecotoxicity Potential (FATEP), Human Toxicity Potential (HTP), Marine Aquatic Ecotoxicity Potential (MAETP). The best value for GWP, 828.86 kg CO_2-Equiv./ton and for AP 2.97 Kg SO2-Equiv./ton was obtained when benzene is produced from reformate. The best values for the impact categories related to lethal concentration (FAETP, HTP, MAETP) is obtained when benzene is obtained from pyrolysis.

The most significant contributors to the above mentioned impact categories are the raw materials (toluene and hydrogen) production processes. For the base case, toluene was produced from reformate, hydrogen was produced from natural gas steam reforming and the steam requested by the process is produced from natural gas. In order to improve the environmental performance of the base case the attention was focused on the toluene and hydrogen production processes considering alternative routes (e.g. toluene from pyrolysis, hydrogen from steam reforming of natural gas and toluene from pyrolysis, hydrogen from steam reforming of heavy fuel oil). The conclusion of such assumptions is that the environmental impact is even worst.

Nomenclature
ADP - Abiotic Depletion Potential
AP - Acidification Potential
E- heat exchanger
EP - Eutrophication Potential
F-Flash (separator)
FAETP - Freshwater Aquatic Ecotoxicity Potential
FH- fired heater
GWP - Global Warming Potential
HDA - hydrodealkylation of toluene
HTP - Human Toxicity Potential
LCA - Life Cycle Analysis
LCI - Life Cycle Inventory
MAETP - Marine Aquatic Ecotoxicity Potential
ODP - Ozone Layer Depletion Potential
PCOP - Photochemical Ozone Creation Potential
Pygas - Pyrolysis Gasoline
S-stream
SRK - Soave Redlich Kwong
T – tower (distillation column)
TETP - Terrestrial Ecotoxicity Potential
TDP - Toluene Disproportionation Process

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COOLING WATER NATURAL DRAFT TOWER MODELLING AND MULTIPERIOD SIMULATION

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Abstract

Most industrial processes have a significant amount of heat that must be removed effectively in the environment, using air or water as coolant. Air coolers, once-through cooling water systems and re-circulating cooling water systems, are all used for the rejection of wasted heat to the environment. Of these methods, recirculating cooling water systems are by far the most common because recirculating cooling water systems can conserve freshwater and reduce thermal pollution, relative to once-through systems. The main components of the system are: cooling tower and heat exchanger network (HEN). In this work wet natural-draft cooling tower (NDWCT) performance prediction is accomplished using Merkel (Me) heat and mass transfer method.

Key words: water cooling systems, natural draft wet-cooling tower, Merkel number.

1. Introduction

Several factors make water the most efficient way of dissipating unwanted heat: it is readily available and inexpensive and it can carry large amount of heat. Cooling water systems can be classified in three broad categories:

- once through system (the cooling water passes through the heat exchanger network only once);
- closed recirculating system (cooling water is used in a repeatedly cycle);
- open recirculating system (used the evaporative cooling mechanism to remove the heat energy from an industrial process into the atmosphere).

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In evaporative cooling, water is cooled while it flows over a fill in a cooling tower, in countercurrent with the air stream. Cooling towers are employed to re-use the water amount for cooling the hot process streams from the industrial site, without discharging it in the environment. In general, the open recirculating cooling water system is the most common for industrial plants.

We need cooling towers in almost all the process industries, i.e. petrochemical industries, air conditioning systems, food industries. They can be classified according to the type of draft through the tower:

- natural draft cooling tower (draft is established by the inside hotter air buoyancy compared to the air from outside of the tower)
- mechanical draft cooling tower (draft is established by fans that force or draw the air inside the tower). There are two types of mechanical draft cooling tower: forced and induced.

2. Mathematical model for NDWCT

There have been several large-scale experimental studies developed describing heat and mass transfer fundamentals in a cooling tower. A significant number of these were carried out to study heat and mass transfer processes in a wet cooling tower. The purpose of these studies was to develop a complete and accurate mathematical model in order to predict NDWCT performance. The most known model, proposed and verified, is the Merkel model [1]. Another model, with a greater accuracy, was proposed by Poppe [2]. The Merkel model has been widely adopted by industrial plants and integrated into all standards regarding cooling towers, due to its simplicity.

Cooling water with air operation relies on basic principles. Air movement is essentially dependent upon the difference in density between the entering air and that one from the tower. In this case, the water is in direct contact with the air. Cooling is the effect of sensible and latent heat transfer. NDWCT mathematical formulation involves applying one of the above models with a simple hydrodynamic calculation and treating one single area from the tower - the fill zone. Inside the NDWCT take place two transfer operations: evaporation (heat transfer operation) and absorption (mass transfer operation). During these two operations the water is cooled and air humidity and temperature are increased. The mathematical model is limited to one dimension. Following assumptions are considered [3]:

- the water temperature is taken as average value at each vertical point;
- temperature and flow gradients for air are neglected;
- a thin film of air saturated with water vapor at a temperature of the water is at the water-air interface.

2.1. Heat and mass transfer equations

Heat and mass balance equations are written for an infinitesimal control volume as you can observe in Figure 1.

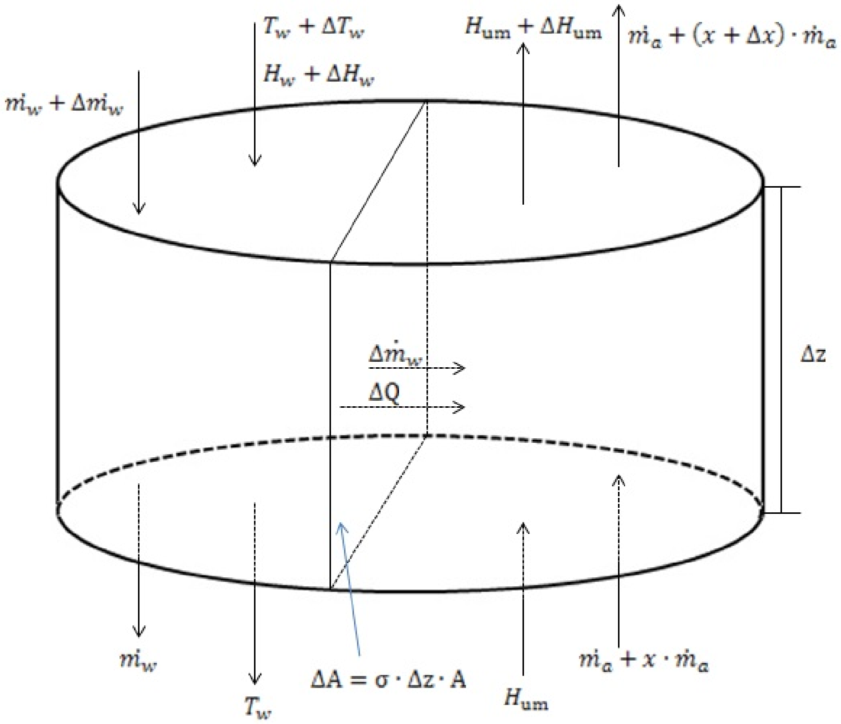

Fig. 1. Control volume element

Mass balance equation

Water flow at the outlet of the volume element can be written as a function of water flow at the entrance of the volume element:

$$\dot{m}_{w|z+\Delta z} = \dot{m}_w|z - \frac{d\dot{m}_w}{dz} \cdot \Delta z \qquad (1)$$

For the air flow we can write a similar equation:

$$(\dot{m}_a + x \cdot \dot{m}_a)_{|z+\Delta z} = (\dot{m}_a + x \cdot \dot{m}_a)|z + \frac{d(\dot{m}_a + x \cdot \dot{m}_a)}{dz} \cdot \Delta z \qquad (2)$$

This can be rearranged to equation (4):

$$-\frac{d\dot{m}_w}{dz} \cdot \Delta z = \frac{d(x \cdot \dot{m}_a)}{dz} \cdot \Delta z, \forall \Delta z \neq 0 \qquad (3)$$

$$-\frac{d\dot{m}_w}{dz} = \frac{\dot{m}_a \cdot d(x)}{dz}, \forall \Delta z \neq 0 \qquad (4)$$

Heat balance equation for air phase

Based on heat transfer principles equation (5) represents the heat balance for gaseous phase:

$$(\dot{m}_a + x\cdot\dot{m}_a)\cdot\left\{c_{pa}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)+x\cdot\left[(H_v+c_{pv}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)\right]\right\}+k\cdot(T_w-T_a)\cdot\frac{dA}{dz}\cdot\Delta z+$$

$$+H_v\cdot\frac{d\dot{m}_w}{dz}\cdot\Delta z=\left[\dot{m}_a+\left(x+\frac{dx}{dz}\cdot\Delta z\right)\cdot\dot{m}_a\right]\cdot\left(\begin{matrix}\left\{c_{pa}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)+x\cdot\left[(H_v+c_{pv}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)\right]\right\}+\\ \dfrac{d(\left\{c_{pa}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)+x\cdot\left[(H_v+c_{pv}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)\right]\right\}}{dz}\cdot\Delta z\end{matrix}\right) \quad (5)$$

where: $H_{um}=c_{pa}\cdot T_a+x\cdot(H_{v,0}+c_{pv}\cdot T_a)$ (6)

$$H_v=H_{v,0}+c_{pv}\cdot T_w \quad (7)$$

Rearrange the above equation into:

$$\dot{m}_a\cdot\frac{dH_{um}}{dz}\cdot\Delta z=K_T\cdot(T_w-T_a)\cdot\frac{dA}{dz}\cdot\Delta z+H_w\cdot\frac{d\dot{m}_w}{dz}\cdot\Delta z \quad (8)$$

The heat balance equation for air phase is obtain by simplifying equation (8) by Δz:

$$\dot{m}_a\cdot\frac{dH_{um}}{dz}=K_T\cdot(T_w-T_a)\cdot\frac{dA}{dz}+H_w\cdot\frac{d\dot{m}_w}{dz} \quad (9)$$

The right term of equation (9) contains both the contribution of mass and heat transfer. $K_T\cdot(T_w-Ta)\cdot\frac{dA}{dz}$ represents the heat transfer effect, and the second product $H_w\cdot\frac{d\dot{m}_w}{dz}$ represents the mass transfer effect.

Total heat transfer equation

Based on figure 1 it can be written that:

$$(\dot{m}_a+x\cdot\dot{m}_a)\cdot H_{um}+(\dot{m}_w+\frac{d\dot{m}_w}{dz}\cdot\Delta z)\cdot c_{pw}\cdot(T_w+\frac{dT_w}{dz}\cdot\Delta z)=$$

$$=\left[\dot{m}_a\cdot c_{pa}\cdot(T_a+\frac{dT_a}{dz}\cdot\Delta z)+c_{pw}\cdot\dot{m}_a\cdot(x\cdot T_a+\frac{d(x\cdot T_a)}{dz}\cdot\Delta z\right]+\dot{m}_w\cdot c_{pw}\cdot T_w \quad (10)$$

(x·T) product can be neglected. This equation can be rearranged and the total heat transfer equation is obtained:

$$\dot{m}_a \cdot \frac{dH_{um}}{dz} - \frac{d(\dot{m}_w \cdot c_{pw} \cdot T_w)}{dz} = 0 \quad (11)$$

where $c_{pw} \cdot T_w = H_w$. (12)

Equation (12) can be written as:

$$\dot{m}_a \cdot \frac{dH_{um}}{dz} - \frac{d(\dot{m}_w \cdot H_w)}{dz} = 0 \quad (13)$$

2.2. Merkel number

Heat and mass transfer phenomena can switch into a single equation based on the air-water enthalpy difference from the interface [4]. Driving force for the heat and mass transfer has been reduced to the difference in enthalpy between water and air. Merkel number depends on air flow (via total transfer coefficient) and water flow. Merkel number can be written in terms of enthalpy difference:

$$\mathrm{Me} = \frac{\mathrm{K_m} \cdot \mathrm{A}}{\dot{\mathrm{m}}_\mathrm{w}} = \int_{\mathrm{T_{w,0}}}^{\mathrm{T_{w,i}}} \frac{\mathrm{c_{pw}} \cdot \mathrm{dT_w}}{\mathrm{H}''(\mathrm{T_w}) - \mathrm{H_{um}}} \quad (14)$$

where: $\mathrm{H}'' = \mathrm{c_{pa}} \cdot \mathrm{T_w} + \mathrm{x}'' \cdot \left[\mathrm{H_{v,0}} + \mathrm{c_{pw}} \cdot \mathrm{T_w}\right] = \mathrm{c_{pa}} \cdot \mathrm{T_w} + \mathrm{x}'' \cdot \mathrm{H_v}$ (15)

Merkel number is a dimensionless number used in cooling tower performance prediction. It is analogous to the number of transfer units (NTU). Solver procedure involves numerical integration of Merkel number between the inlet and outlet water temperature. The data needed are: input temperature of water, water and air flow, relative humidity and air temperature at the entrance of the tower and Merkel number. Water outlet temperature is proposed in the beginning and checked after each step of the numerical integration until calculated Merkel number can be compared with the initial one.

3. Case study

A plant requires 10500 m^3/h cooling water removing 125 MW from the HEN. The water leaves the exchangerrs at 38 °C. The cooling water will be cooled in a NDWCT. The design conditions can be observed in table 1. Compute the results of numerical integration in this case study.

Table 1.

Design conditions for NDWCT

Tower height	63 m
Fill height	1.5 m
Cooling water flow rate	10,500 m^3/h
Water inlet temperature	38 °C
Air dry bulb temperature	30.2 °C
Air wet bulb temperature	20.6 °C
Cooling tower basin volume	10,000 m^3
Basin diameter	48.4 m
Minimum radius	14 m
Basin depth	0.5 m

3.1. Methodology

In the subsequent performance calculation Merkel number is known, but the outlet temperature of water is not. In this example the water outlet temperature must be guessed and checked through repetitive looping until calculated Merkel number matches the specified Merkel number within a tolerance of $5 \cdot 10^{-5}$. The exact latent and sensible heat ratio is unknown at any point in the fill zone, only the overall enthalpy is known. Frequently, the air is assumed to be saturated at the outlet and this grant the air outlet temperature proximity.

Solver routine involves the numerical integration using the tool *ode45* in MATLAB® 2012a environment using additional package SIMULIS©, as database and physical-chemical properties calculation server, and a toolbox developed to link the two environments [6].

3.2. Results

After solving the program all the results obtained are shown in Figures 2-5. Cooling limit is becoming smaller as high values for Me number. Knowing that Merkel number contains both the influence of mass and heat transfer, we can say that Me number values decrease with high inlet water temperature values, reducing the outlet water temperature

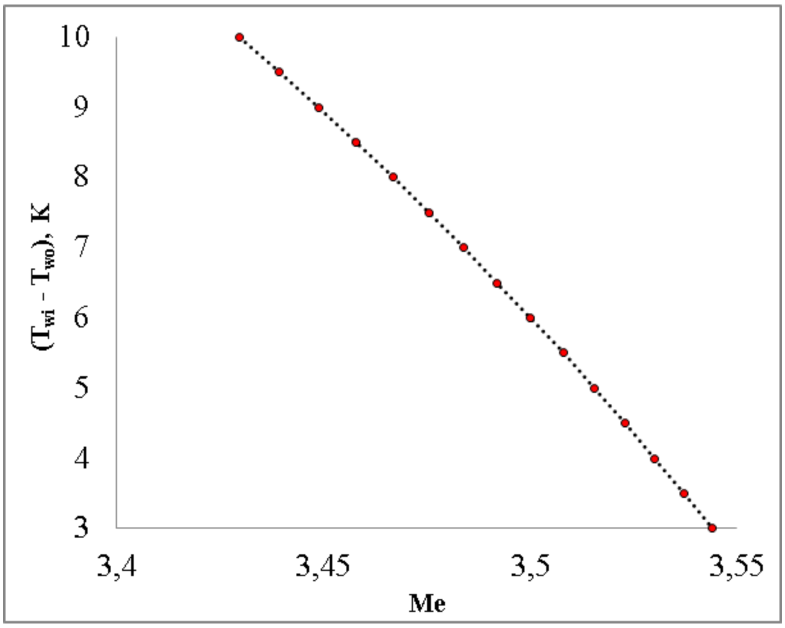

Fig. 2. Cooling range dependence of Me number

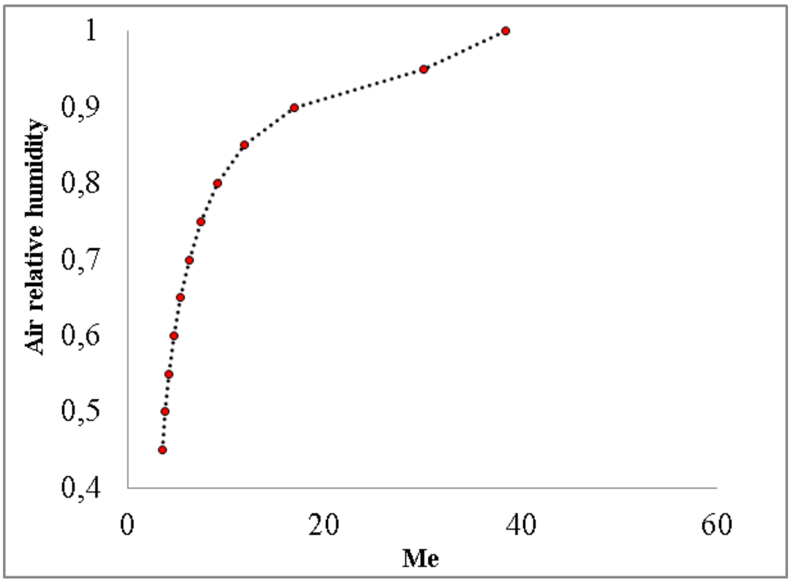

Fig. 3. Air relative humidity dependence of Me number

As the air approaches the saturation point, the cooling process is slowed. At the time the air reaches the saturation level ceases, the cooling process is stopped (as shown in Figure 3).

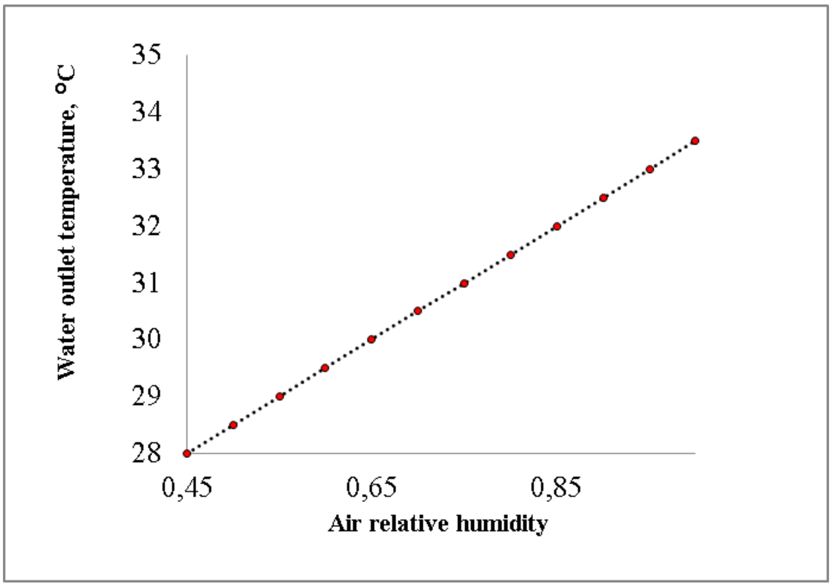

Fig. 4. Water outlet temperature dependence of air relative humidity

High water flowrates speed air enrichment with vapours, making the cooling operation ineffective (as shown in Figure 4).

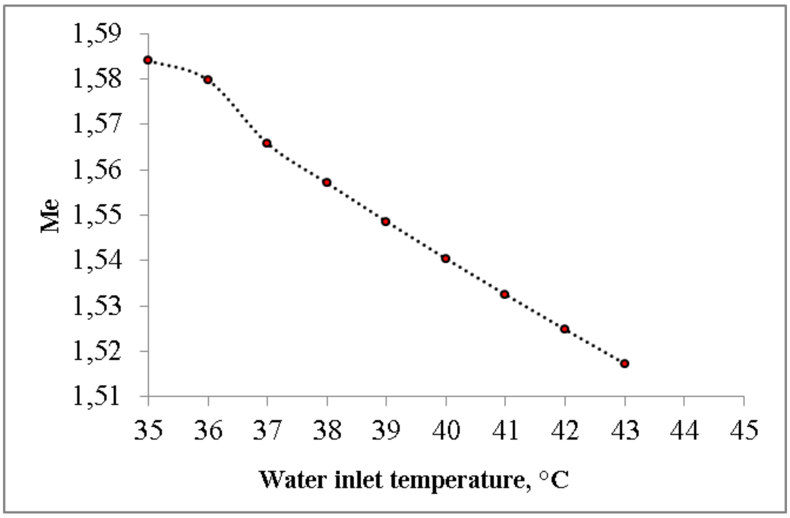

Fig. 5. *Me number dependence of water inlet temperature*

From Figure 5 we can easily observe that Me number decrease for increasing water inlet temperatures. This leads to an ineffective cooling process.

4. Conclusions

A relative simple empirical relation can easily predict NDWCT performance. The temperature and humidity influences on NDWCT performance are investigated. A complete computer program is developed in order to predict NDWCT performance and to determine cooling water outlet temperature. This work helps to develop a complete mathematical model for a better understanding of NDWCT behaviour. This study can leads to a cheaper and more effective cooling operation.

Nomenclature

A - transfer area, m^2
c_p - specific heat, kJ/(kg·K)
H - enthalpy, kJ/kg
K_f - loss coefficient
K_T - total heat transfer coefficient, kW/(m^2·K)
K_M - total mass transfer coefficient, kg/(m^2·s)
$\dot{m}$ - mass flowrate, kg/s
T_a - air inlet temperature, °C
T_{wi} - water inlet temperature, °C
T_{wo} - water outlet temperature, °C
T_{wb} - wet-bulb temperature, °C
x - relative humidity, kg apă/kg aer uscat
z - length, m

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OPTIMAL DESIGN OF 1,1 - DIETHOXY BUTANE PRODUCTION PROCESS

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Abstract

Acetals are additives which improve various fuels properties, such as cetane number, lubricity, biodegradability, flash point. Acetals can be obtained by reacting an alcohol with a suitable aldehyde, in the presence of an acid catalyst. The production of several acetals has been studied at laboratory scale, using conventional reactors, membrane reactors and reactive distillation. However, few studies are concerned with the design, control and economic evaluation of an entire plant.In this article we consider a process for production of 1,1-diethoxy butane by reaction of ethanol with butanal, catalyzed by Amberlyst 47. A simplified model of the Reaction – Separation – Recycle process is used to analyze the feasibility of the process. The economic evaluation is made using literature relationships for capital and operational cost estimation. The complete plant design was achieved using Aspen Plus. Finally, both distillation columns are optimized in order to reduce Total Annual Cost.

Key words: process design, acetal, economic evaluation, column optimization

1. Introduction

The rise of fossil fuel prices, the environmental considerations and energy security concerns give new incentives for the use of renewable sources, development of nuclear power and other energy alternatives. Biodiesel is a renewable biofuel made by the combination of an alcohol (usually methanol) and a vegetable oil, recycled cooking grease or animal fat. Biodiesel is a much cleaner fuel source; it fulfills the energy demand reducing the dependency on oil; it can be easily produced and stored; it increases the lubricity of the engine and the ignition point, reducing the danger of explosion; it improves biodegradability and reduces toxicity. However, there also some disadvantages of using biodiesel: more NO_x compounds and particles emissions harmful to the environment; inferior operability in cold weather; lower energy content and oxidation stability.

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Additives are a potential solution to improve the quality of biodiesel and to overcome the harmful emissions problem. Although metal-based additives could be used, combustion enhancers obtained from renewable sources are the best option [1, 2]. Thus, the literature review shows an increased interest in oxygenated additives with 8 – 10 carbon atoms, such as ethers (di n-pentylether, [3, 4]) or di-ethers (1,1 diethoxy butane, [5,6]).

In a previous article [7], we used a simplified Reaction – Separation – Recycle model of the process to develop a feasible control structure. Then, the process was designed and its controllability was proved by rigorous dynamic simulation. In this article we perform an economic evaluation of the plant and achieve its optimum design by minimizing the total annual cost. The next section presents the reaction kinetics and the physical properties, relevant to design of the reaction and separation sections, respectively. Then, the base case design, optimization procedure and the optimal design are described. The article ends with conclusions.

2. Basis of design

The reaction between butanal and ethanol takes place in liquid phase, in the presence of Amberlyst 47 as an acid catalyst. The reaction is reversible and slightly exothermal. The alcohol (ethanol) can be easily obtained by fermentation from renewable sources such as starch, sugar cane, sugar beet, corn or maize. The aldehyde (butanal) can be obtained by hydroformilation of propylene or by dehydrogenation of n-butanol (available from ABE fermentation).

$$\underset{(E)}{2C_2H_5OH} + \underset{(B)}{C_3H_7-CH=O} \leftrightarrow \underset{(A)}{C_3H_7-CH\left(OC_2H_5\right)_2} + \underset{(W)}{H_2O} \qquad (1)$$

The reaction rate is given by the following relationship [8]:

$$r = k_1 c_E^2 c_B - k_2 c_A c_W \qquad (2)$$

$$k_1 = 1.08 \cdot \exp\left(-\frac{35505}{8.31 \cdot T}\right) \ \frac{\left(m^3\right)^3}{kmol^2 \cdot s \cdot kg_{cat}} \qquad (3)$$

$$k_2 = 1.06 \times 10^5 \cdot \exp\left(-\frac{59752}{8.31 \cdot T}\right) \ \frac{\left(m^3\right)^2}{kmol \cdot s \cdot kg_{cat}} \qquad (4)$$

The dependence of the equilibrium conversion, X_{eq}, versus the reaction temperature, T, is presented in Figure 1, for different values of the Ethanol / Butanal ratio, M_{EB}. The reaction equilibrium is favored by larger ethanol excess and lower temperature. At 40 °C, conversion exceeding 0.75 can be achieved for reactants ratio above 4.

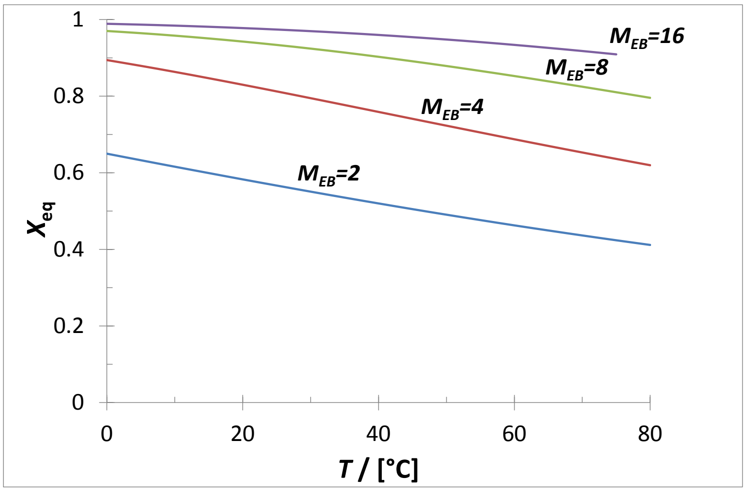

Fig. 1. Equilibrium conversion

Table 1 presents the normal boiling points of the reactants, products and their azeotropes. It can be seen that the reactants (butanal and ethanol) are the lightest components, with close boiling points, and forming several homogeneous azeotropes with water.

Table 1

Boiling points of reactants, products and their azeotropes

Temperature / [°C]	Composition (molar)	Destination
69.55	Butanal (0.748) – Water (0.252)	Recycle
73.15	Ethanol (0.303) – Butanal (0.697)	
74.88	Butanal	
78.15	Ethanol (0.895) – Water (0.105)	
78.31	Ethanol	
94.06	Water (0.881) – 1,1 diethoxy butane (0.119)	Product purification
100.0	Water	
153.69	1,1 diethoxy butane	

Moreover, the water and 1,1-diethoxy butane forma heterogeneous azeotrope, as shown by the *Txy* diagram presented in Figure 2.

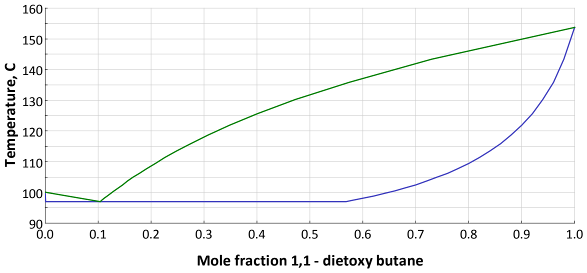

Fig. 2. T-xy diagram of 1,1-diethoxy butane/Water mixture (1.013 bar)

3. Flowsheet and base case design

Being a classical chemical process, the reaction is equilibrium-limited and complete reactants conversion is impossible [9]. Therefore, reactants separation and recycle are necessary. Because the reactants are the lightest components in the mixture, they will be separated and recycled together. Moreover, as water forms several light-boiling azeotropes with the reactants, it will also be present in the recycle stream.

The flowsheet of the plant and the key sizing parameters of the base case are shown in Figure 3. Fresh reactants are mixed with the recycle and sent to the reactor. From the reactor effluent, ethanol and butanal, which are the light components, are removed by distillation and recycled. The recycle contains some amounts of water due to the water-ethanol and water-butanal azeotropes. The bottom of the first distillation column consists of water and 1,1-diethoxy butane. However, water and 1,1-diethoxy butane form an heterogeneous azeotrope. After cooling, two liquid phases are formed and separated in a decanter. The aqueous phase, with very little amounts of 1,1-diethoxy butane, is removed. The organic phase is sent to the second distillation column. The bottom product is high purity 1,1-diethoxy butane. The distillate consists of the 1,1-diethoxy butane -water azeotrope, which is recycled back to the decanter. Detailed stream results are presented in Table 2.

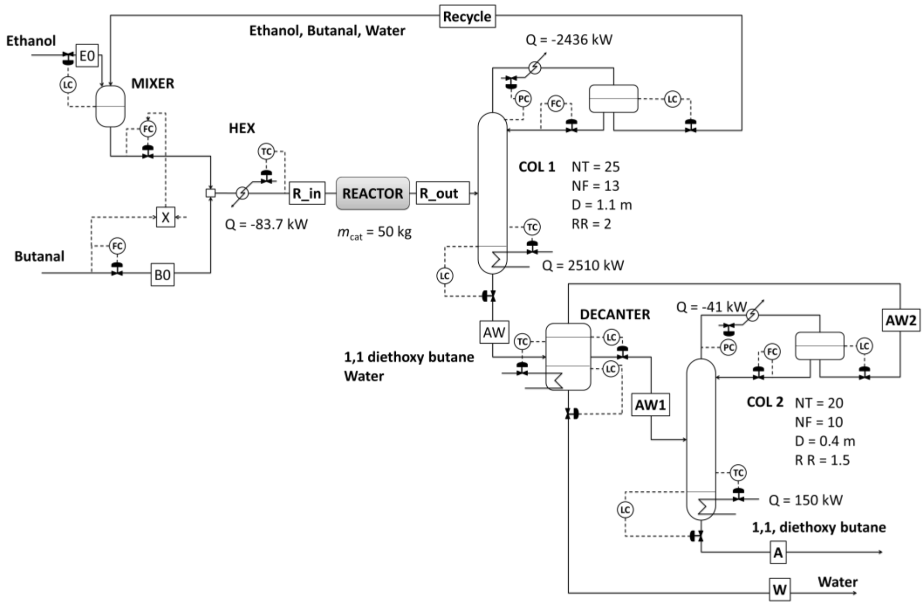

Fig. 3. Flowsheet and plantwide control

Table 2.

Stream table – base case

	B0	E0	R_in	R_out	Recycle	AW	AW1	AW2	A	W
T / [C]	19.9	19.9	40.0	63.8	78.4	99.1	30.0	92.2	156.1	30.0
P / [bar]	1.00	1.00	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
F /[kg/h]	721.1	967.1	5083.8	5083.8	3395.6	1688.2	1507.5	45.67	1461.9	226.3
F / [kmol/h]	10.00	22.5	108.7	98.7	76.2	22.5	11.44	1.43	10.0	12.5
Mole frac.										
A	0.000	0.000	0.000	0.101	0.000	0.444	0.886	0.098	0.999	0.000
E	0.000	0.89	0.692	0.559	0.724	0.001	0.006	0.048	0.000	0.002
B	1.000	0.000	0.173	0.089	0.115	0.000	0.000	0.001	0.000	0.000
W	0.000	0.11	0.135	0.251	0.161	0.555	0.108	0.853	0.001	0.998

4. Economic Evaluation

The Cost of Investment (CAPEX) and the Cost of Operation (OPEX) were estimated using the relationships given by Dimian, [10]. These consider equipment dimensions, operating pressure, used material and correction factors for CAPEX calculation. The equations for installed cost of equipment are given below. The capacity data are expressed in metric units. The M&S (Marshall and Swift Cost Index) factor was estimated at a value of 1476.7 for all the calculations. The construction material used for all the equipment was carbon steel (CS).

The installed cost of pressure vessels, columns and reactor follows the relationship below:

$$\mathit{Installed\ Cost}\ (\$) = \left(\frac{M\&S}{280}\right)\cdot\left(957.9\cdot D^{1.066}\cdot H^{0.82}\cdot(2.18+F_c)\right) \tag{5}$$

Both D (diameter) and H (height) are expressed in meter. The factor $F_c = F_m \cdot F_p$ takes into account the material F_m and pressureF_p. The pressure factor F_p factor can be correlated by the following expression:

$$F_p = 1 + 0.0074\cdot(P-3.48) + 0.00023\cdot(P-3.48)^2 \tag{6}$$

with P in bar. As the pressure vessels were considered made from carbon steel, the material factor is 1.0.

Installed Cost for Trays is given by the following relationship:

$$\mathit{Installed\ Cost}\ (\$) = \left(\frac{M\&S}{280}\right)\cdot 97.2\cdot D^{1.55}\cdot H\cdot F_c \tag{7}$$

For standard 24 in. tray spacing the overall correction factor is$F_c = F_t + F_m$, where $F_t = 0$(sieve trays) and $F_m = 1.0$(for carbon steel).

Heat exchangers are designed as shell-and-tubes, with the cost calculated as:

$$\mathit{Installed\ Cost}\ (\$) = \left(\frac{M\&S}{280}\right)\cdot\left(474.7\cdot A^{0.65}\right)\cdot(2.29+F_c) \tag{8}$$

The heat exchanger area A is in m^2, and $20<A<500$ m^2/shell.

$$F_c = F_m \cdot (F_d + F_p) \tag{9}$$

where $F_m=1$ (carbon steel);
$F_d = 1$ for floating head and $F_d = 1.35$ for kettle reboilers;
$F_p = 0$ for $P<10$.

The resulting CAPEX for the base case design is given in the following table.

Table 3

Estimated Cost of Investment

Equipment	*Installed cost/ [$]*
Vessels	177 691
Col 1	162 992
Col 2	55 442
Reflux vessels	111 922
Decanter	33 772
Reactor	39 345
Trays	10 771
Heat Exchangers	742 410
Total CAPEX	**1 334 000**

Operational cost includes cooling water and steam cost given in table 4.

Table 4

Utility prices

Utility	*Price*	*OPEX/ [$/year]*
Cooling water	0.08 $/m^3	156360
Heating (steam)	0.000005 $/kJ	389 595
Total OPEX		**545 955**

Considering a 3 year term of CAPEX repayment, the estimated total cost is about 2 M$/year.

5. Optimization Procedure

The objective function is the Total Annual Cost (TAC), calculated as described before. Inspection of Table 3 shows that the distillation columns (including reboilers and condensers) have the most important contribution to TAC, while the reactor is relatively cheap. Therefore, by minimization of the TAC is achieved by minimization of the columns TAC. For each column, the (design) decision variables are the number of stages, the location of the feed stage and the reflux ratio.

A. Reactants column

The reactants column (COL-1, Fig. 3) separates the reactants (to be recycled) from the products. However, due to existence of several azeotropes (Table 1), the recycle contains a certain amount of water which has a detrimental effect on the conversion achieved by the chemical reactor. Therefore, columns with few trays will lead to a high operating cost due to large amounts of water being recycled, which give low conversion and therefore large recycle rates. On the other hand, over-purifying the recycle is also expensive with limited benefit regarding the reactor conversion. As the interactions between reaction, separation and recycle are complex the optimisation was performed by considering the CAPEX and OPEX of the entire loop: column (including shell, trays, reboiler and condenser), reactor and storage vessels.

The optimization results (Fig. 4) shows that the reactants column should be operated a low reflux ratio (RR = 0.5). Moreover, fewer trays should be used, compared to the base case.

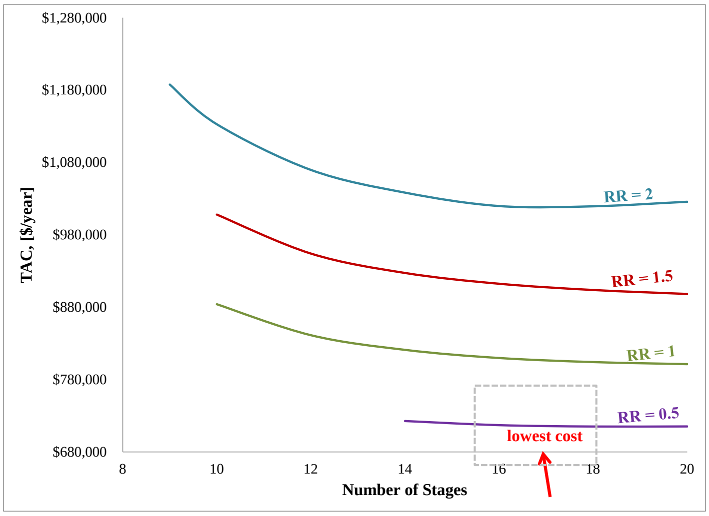

Fig. 4. Total Annual Cost (TAC) depending on Column Reflux Ratio (RR) and Number of Stages (Column I)

Compare also the lowest value obtained for I Sequence including column I (715240$/year) with the original sequence cost of 1 037 779 $/year when RR = 2, NTT = 25 and FS = 13 (Table 5).

Table 5

Lowest TAC for each reflux ratio considered – Column I

RR	NTT	Optimized Feed Stage	Lowest TAC/[$/year]
2	18	8	1 019 515
1.5	20	12	898 408
1	20	11	801 406
0.5	18	7	715 240

B. Products Column

The optimisation of the products column (COL-2) was achieved by considering the CAPEX and OPEX of the whole product separation loop: heat exchanger,decanter vessel, column (shell, trays, condenser and reboiler.

Fig. 5 shows the dependence of the TAC on reflux ratio, number of stages and the feed stage.

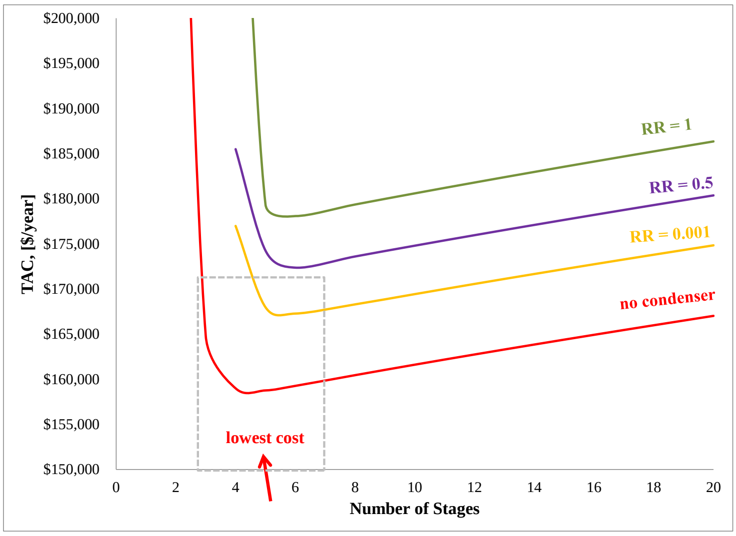

Fig. 5. Total Annual Cost (TAC) depending on Column Reflux Ratio (RR) and Number of Stages (Column II)

It turns out that the optimal column should operate as a stripper – no condenser, with the liquid feed on the first stage. Note that the purity of the top product is not important, as it is recycled back to the liquid-liquid separation. Moreover, one function of the condenser (providing the distillate product as a liquid) is necessary, as it is achieved by the heat-exchanger placed before the liquid-liquid separation.

Best values of the simulation are given in the table below. The lowest TAC for each reflux ratio considered is showed.

Table 6

Lowest TAC for each reflux ratio considered -Column II

RR	NTT	Optimized Feed Stage	Lowest TAC/[$/year]
1	6	4	178085
0.5	6	3	172368
0.001	6	2	167281
no condenser	5	1	158766

Compare the lowest value obtained (158 766$/year) with the original sequence cost of 192 223 $/year when RR = 1.5, NTT = 20 and FS = 10 (Table 6).

The flowsheet of the final (optimized) design is presented in Figure 6, together with the main design parameters and key unit sizing elements. Detailed stream table is shown in Table 7.

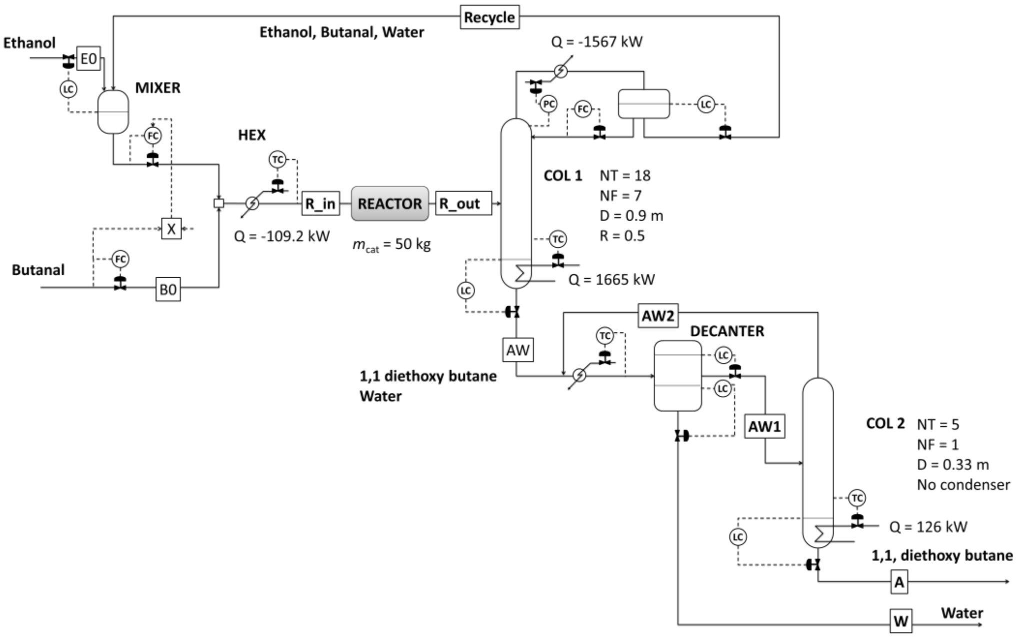

Fig. 6. Optimized design – flowsheet and plantwide control

Table 7

Stream table – Optimized design

	B0	E0	R_in	R_out	Recycle	AW	AW1	AW2	A	W
T / [C]	19.9	19.9	40.0	60.6	78.6	99.1	30.0	102	156.1	30.0
P / [bar]	1.00	1.00	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
F / [kg/h]	721.1	967.1	5802.8	5082.8	4114.6	1688.2	1514.9	53	1461.9	226.3
F / [kmol/h]	10.00	22.5	129.7	119.7	97.18	22.5	11.49	1.49	10.0	12.5
Mole frac.										
A	0.000	0.000	0.000	0.085	0.000	0.444	0.886	0.126	0.999	0.000
E	0.000	0.89	0.637	0.523	0.644	0.001	0.006	0.047	0.000	0.002
B	1.000	0.000	0.159	0.089	0.110	0.000	0.000	0.002	0.000	0.000
W	0.000	0.11	0.202	0.302	0.243	0.555	0.108	0.824	0.001	0.998

6. Conclusions

The main objective of the present study was fulfilled: anoptimized plant that produces 1,1 diethoxy butane (a valuable biodiesel additive) was designed.

The reaction can be performed in the presence of an acid catalyst, in a CSTR or PFR. Because the reaction is slightly exothermic, adiabatic reactor operation is possible.

The separation section consists of two distillation columns. The first column separates the reactants which are recycled, together with some amounts of water due to azeotropes formation. The separation of 1,1-diethoxy butane / water mixture involves breaking their azeotrope, which is achieved by taking advantage of azeotrope heterogeneity through liquid-liquid separation.

By using a simple reactor – separation – recycle model of the plant, the economic evaluation was performed using literature relationships that use pressure, material factor, correction factor etc. But, in order to achieve a lower total annual cost plant needed to be optimized. After optimizing the products separation column it was proven that it needs no condenser. So, the cost decreases to about 18 %. First column optimization leads to a cost decrease to about 31%.

The approach presented in this study can be applied to any process in order to lower the investment cost, as well as the operational cost.

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KINETIC STUDY ON THE CONTROLLED RELEASE OF METRONIDAZOLE FROM ORAL DOSAGE FORMS

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Abstract

This paper presents the results of a simulation study regarding the release kinetics of metronidazole from polymeric supports, by using diffusion models. The validity of the selected models is proved by comparing the predictions of the models with the experimental profiles obtained in simulated intestinal fluid (pH 7.4) and reported in the recent literature. The predictions obtained from this study are useful to improve the oral administration of the considered antibiotic and guide further investigations.

Key words: Controlled release, Metronidazole, Diffusion models

1. Introduction

Clinicians have long recognized the therapeutic benefit of being able to administer a drug that offers extended release or location targeted drug release within the gastro-intestinal tract. As a main tool to control the oral drug release rate from the formulations, polymeric matrices with specific properties are often used. Controlled release systems have been developed to improve the temporal and spatial presentation of drug in the body, to protect drug from physiological degradation or elimination and to improve patient compliance [1]. When designing controlled-release systems, it is important to identify and understand particular mechanisms involved in the release process. Often, more than one mechanism is involved at a given time or different mechanisms may dominate at different stages of the drug delivery process. The controlled release of metronidazole, which is a nitroimidazole antibiotic medication, from numerous matrix-type and polymeric-coated formulations has been widely investigated, because it is well absorbed orally, with a plasma elimination half-life ranging from 6-7 hours [2].

Asnaashari et al. [3] reported results for the evaluation of metronidazole sustained release. Hydroxyl propyl methylcellulose (HPMC), psyllium and carbopol in different concentrations were used as floating agents. Kinetically,

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among the 10 assessed models, the release pattern of metronidazole from the tablets fitted best to Power law, Weibull and Higuchi models [3].

Emara et al. [4] studied the controlled release of metronidazole from various synthetic and natural polymers, namely: HPMC, carbopol 974P, sodium alginate, locust gum and guar gum. In their study, the release pattern of metronidazole from the tablets fitted best to Zero order and Hixson & Crowell Cube-Root models [4].

Our research was based on the experimental results reported by Mourya et al. [2] for the release of metronidazole from HPMC tablets in phosphate buffer (pH 7.4). The aim of this paper is to evaluate the release kinetics of metronidazole in simulated intestinal fluid.

2. Drug release modelling

Model dependent methods are based on different mathematical functions, which describe the dissolution profile. The dissolution profiles are evaluated depending on the derived model parameters. The model dependent approaches include zero order, first order, Higuchi, Hixson-Crowell, Korsmeyer-Peppas, Baker-Lonsdale, Weibull, Hopfenberg, Gompertz and regression models.

More appropriate to the results reported by Mourya et al. [2], were Korsmeyer-Peppas, Fick’s diffusion equation and Higuchi equation.

Korsmeyer-Peppas model

This model, also known as the Power Law, has been used frequently to describe the drug release from different pharmaceutical release dosage forms [2-3].

$$\frac{M(t)}{M_\infty} = k \cdot t^n \qquad (1)$$

where k is a constant incorporating structural and geometric characteristics of the drug dosage form and n is the release exponent, indicative of the drug release mechanism. It is generally used when the release mechanism is not well known . To find out the exponent of n, the portion of the release curve where $Mt / M\infty < 0.6$, should only be used. [5,8].

Fick’s diffusion equation

The dosage forms represented by tablets can be considered as sheets. For the diffusion from a sheet and constant diffusivities, the equation takes the form [7]:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \qquad (2)$$

The initial and boundary conditions are written as follows:

$$t = 0;\ -L \le x \le +L;\ C = C_0$$
$$t > 0;\ -D\left(\frac{\partial C}{\partial x}\right)_L = h\left(C_s - C_\infty\right) \tag{3}$$

When the rate of stirring of the release medium is high enough, the value of the mass transfer coefficient is practically infinite, and the drug concentration on the surface reaches its value at equilibrium as soon as the dosage form is put in contact with the liquid.

In this case, the amount of drug released after a period of time *t*, as a fraction of the corresponding quantity after infinite time, is calculated from the equation [6]:

$$\frac{\mathrm{M(t)}}{\mathrm{M}_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(-\frac{(2n+1)^2\cdot\pi^2}{4L^2}\mathrm{D}\cdot t\right) \tag{4}$$

Higuchi equation

The Higuchi equation describes the release of a drug from a polymeric matrix as a square root of a time dependent process based on a Fickian diffusion [5-6]:

$$\mathrm{M(t)} = k_H\sqrt{t} \tag{5}$$

The parameter of the model is the release rate constant, k_H.

3. Results and discussion

By fitting the experimental data reported by Mourya et al. [2], we established the parameters of Korsmeyer – Peppas model for the three formulations of tablets, with the characteristics given in Table 1.

Table 1.

Composition of HPMC tablet of metronidazole [1]

Ingredients, mg	F1	F2	F3
Metronidazole	500	500	500
HPMC	50	50	70
Disintegrant (Corn starch 1500)	30	50	30
Sodium lauryl sulphate	10	10	10
Microcrystalline celulose	25	25	25
Sodium dihydrogen phosphate	2.5	2.5	2.5

As seen in the Table 1, the composition of the three formulations is almost similar. The only differences regard the quantities of HPMC and disintegrant. Thus, no significant differences between the calculated parameters are expected. The values of these calculated parameters are given in Table 2.

Table 2.

Korsmeyer-Peppas parameters

Formulation	k, h^{-n}	n
F1	0,3363	0,599
F2	0,3209	0,572
F3	0,2643	0,488

Because the values of n, which characterizes the release mechanism of drug, are appropriate of 0.5, we used diffusion models.

Considering the Fick's diffusion equation, we established the effective diffusivities of metronidazole from tablets, by fitting the same experimental data, assuming an infinite value of the mass transfer coefficient (the release medium is considered to be perfectly stirred) [7].

On the basis of the calculated effective diffusivities, the predictions of the mathematical model were calculated.

Table 3.

Effective diffusivities of metronidazole from the three formulations of tablets

Formulation	$D_{eff} \cdot 10^{10}$, m^2/s
F1	1,667
F2	1,333
F3	1,194

For the Higuchi model, because the experimental data showed a two step release profile, composed of an initial burst followed by slow release, we have calculated the values of the constant k_H for two time intervals (0-1h and 1-8h).

Table 4.

Higuchi constants calculated for t<1 h and for 1h<t<8h

Formulation	k_h, % of $M_{inf} \cdot h^{-0.5}$
F1	t<1h; 55.40 1h<t<8h; 19.13
F2	t<1h; 53.72 1h<t<8h;15.27
F3	t<1h; 53.72 1h<t<8h;10.64

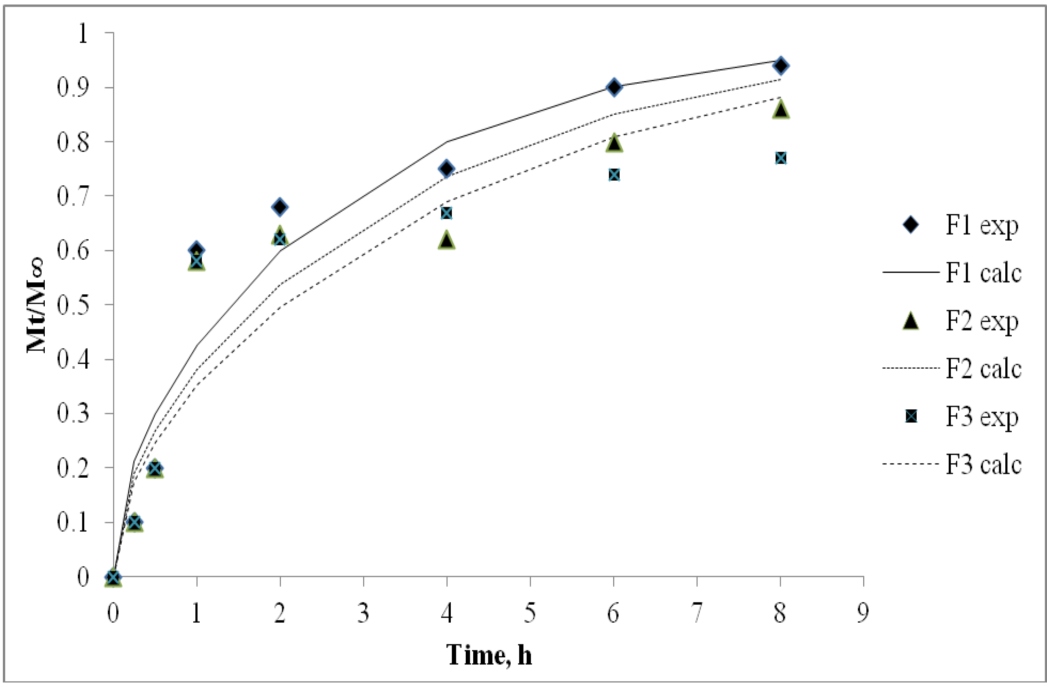

Fig.1. The fraction of drug released after a period of time *t*, calculated with the diffusion model, for formulations F1, F2 and F3

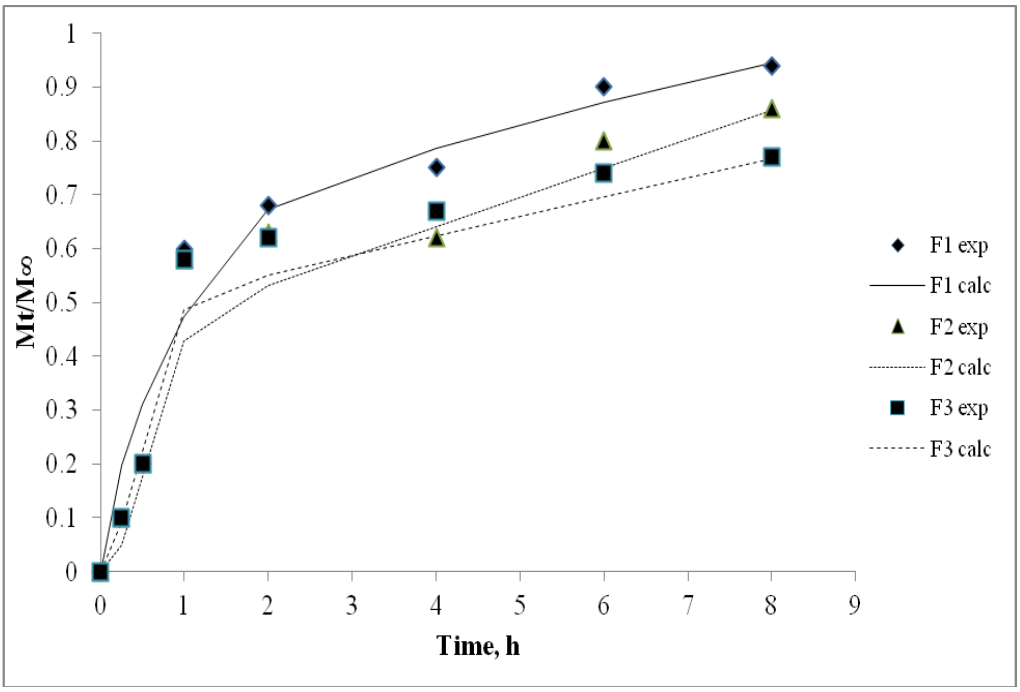

Fig.2. The fraction of drug released after a period of time *t*, calculated with Higuchi model for formulations F1, F2 and F3

4. Conclusions

In our study the experimental results reported by Mourya et al. [2] were considered for the release of metronidazole from hydroxyl propyl methyl cellulose (HPMC) tablets in phosphate buffer. The release rate exhibits two steps, beginning with a fast delivery over the first hour, followed by a slower desorption during the next 7 h. It was found that the kinetic Higuchi model gives the best predictions.

Nomenclature

C - drug concentration
C_0 - drug initial concentration
C_s - drug solubility
C_e - drug concentration at liquid interface at equilibrium
D – diffusivity
D_{eff} – effective diffusivity
h – mass transfer coefficient
k_h - release rate constant for the Higuchi model in the dissolution medium
M_t - amount of drug released after a period of time *t*
M_∞ - amount of drug released after infinite time

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NEW DEVELOPMENT OF CHEMICAL ENGINEERING CURRICULUM AND MULTIMEDIA AIDED TEACHING METHODS IN UNIVERSITY POLITEHNICA OF BUCHAREST

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Abstract
Chemical engineering curriculum for undergraduate education in University POLITEHNICA of Bucharest was analysed and several proposals were formulated in order to adept it to the nowadays demands. A collaborative project between University POLITEHNICA of Bucharest and SIVECO S.A. intended to develop the quality of teaching based on the experience gained by the staff at the Faculty of Applied Chemistry and Materials Science, and by using multimedia tools and animations. The paper presents the main results and also the feed-back obtained from a group of 210 students that participated to training courses based on the new development of the curriculum.

Key words: chemical engineering education, multimedia applications

1. Introduction

Chemical Engineering is a branch of engineering that focuses on designing, constructing, implementing, operating and managing process plants and systems [1].

The working environment and the job market for chemical engineers have evolved continuously during the last two decades, as a consequence of the globalization of the world economy. In many countries, less than 25% of the recent graduates are employed in the conventional chemical and petroleum industries [2].

Most of the graduates are recruited in different domains, which have discovered recently the suitability of hiring chemical engineers [3,4]. Chemical

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engineers work in pharmaceuticals, healthcare, pulp and paper, food processing, microelectronics, electronic and advanced materials, polymers, business services, biotechnology, environmental health and safety industries. All the employers are demanding a greater level of competencies from engineers—versatility in a range of areas, not just the core technical domain [5].

Therefore, the engineering education has to face enormous challenges in order to provide the students with relevant engineering knowledge and skills, as well as those aspects of their education that are relevant for the more flexible, interdisciplinary and intercultural nature of chemical engineering work [2].

After the approval of the joint Declaration of the European Ministers of Education in Bologna in 1999 [6] the universities of Romania adopted new Bologna three-cycle study system: undergraduate, graduate and postgraduate.

The Chemical Engineering undergraduate programme of the University POLITEHNICA of Bucharest last 4 academic years (8 semesters), with 60 ECTS each (total 240 ECTS).

The role of the 1st cycle is to give the students basic knowledge and necessary abilities in the engineering practice.

According these demands, the Centre for Technology Transfer in the Process Industries from the University POLITEHNICA of Bucharest together with SIVECO S. A. built a project intended to develop the quality of teaching in chemical engineering, based on the experience gained by the staff at the Faculty of Applied Chemistry and Materials Science. The project proposed to make improvements in contents and teaching methodologies for the courses: Physical Chemistry, Chemical Engineering Fundamentals, Unit Operations and Chemical Reactors.

In this paper, the development and implementation of the improved teaching process in these courses are presented.

2. Improving quality of teaching and learning in chemical engineering

The curriculum for Chemical Engineering degrees teaches students a wide range of knowledge and skills to be able to undertake this variety of tasks, including classes on core concepts and fundamentals, with incorporation of specialist material in the later years of the course [1].

In the past, the most common form of teaching in engineering classes was lecturing and for many professors lecturing was synonymous with teaching. Lecturing can be an effective, efficient, and satisfying method for both professors and students. Yet many lectures did not satisfy learning principles and was not conducive to student learning. [7].

Based on student reviews and course evaluations, the specific issues from a student perspective are represented by: perception of a high (often too high) work-load, lack of ‘integrated’ teaching and learning, failure to identify relevance of certain courses in the overall programme, chronic dissatisfaction with the ‘quality’ of the learning experience.

From the staff perspective, the key issues are: a need to promote ‘learning’ over ‘teaching’, shifts in employer expectations, increasingly broader employment options, diversity of student background and choice, new technological developments and the impacts of information technology, need for a student-centred rather than a content-driven approach (since students are the immediate beneficiaries of the education process) [5].

The main changes introduced in the last years in the chemical engineering courses at University POLITEHNICA of Bucharest, to promote the teaching–learning process, were focused on using formative continuous assessment, increasing feedback and promoting collaborative learning.

Maybe more intense than in other domains, chemical engineering curricula is based on average high school knowledge in a wide range of subjects: mathematics, physics, chemistry, computer using skills. The diversity of topics and the ever growing need for updated information lead to the necessity of using ICT tools along the entire educational process.

The students’ general opinion participating in the surveys organized in our faculty revealed a growing demand for easier solution identification for complex technical issues and quicker adaptability to team working [8].

Improved curricula for chemical engineering education and a portal designed for teaching by means of multimedia application were realised in the Faculty of Applied Chemical Engineering from University POLITEHNICA of Bucharest by a collaborative project between the Centre of Technology Transfer in Process Industries and SIVECO Romania. In the frame of this project some modifications were made in the content of four courses: Chemical Engineering Fundamentals, Physical Chemistry, Unit Operations and Chemical Reactors.

As an example, we may mention the improvement of Chemical Engineering Fundamentals, course which has as principal objective to form the abilities necessary to solve mass and energy balances. Apart from classical applications from the chemical and petrochemical industries, the content of this course was improved by introducing examples for mass balances from the fields of biotechnologies and medical engineering such as: mass balances for the separations of streptomycin and kanamycin by extraction and filtration from the fermentation broth, mass balance for haemodialysis, mass balance for a bioreactor, analysis of the flow through a restricted blood vessel, by using Bernoulli equation, as an example of energy balance. These applications indicate that the conceptual instruments of the chemical engineering are useful in wide activity areas.

Another example can be given from the content of Unit Operations course. The main modifications consist in the introduction of software tools to establish the feasibility of separation schemes using residual curve maps and for the design of the separation columns.

As reported by Klemes et al.[9], the level of understanding rises starting from listening to a lecture (5%) to reading (10%), audio-visual (20%), demonstration (30%), discussion (50%), practice by doing (75%) and teach others (90%).

According these conclusions, an important objective of the above mentioned project was to create animations, which are considered very useful multimedia elements in the engineering education. The aim of animations was to improve the quality of teaching and learning because they facilitate the understanding of the mechanisms of physical and chemical phenomena, the equipment design and operation. In the frame of the project, 35 animations were realized (Table 1) and included in the video-courses. Some examples are: comparative presentation of the laws of ideal gas in 3D diagram, reversible and irreversible processes, Gibbs diagram and Carnot cycle for Physical Chemistry, developing a technology, temperatures profiles and heat balance of a double pipe heat exchanger, non- steady state heat balance for a mixed vessel for Chemical Engineering Fundamentals, modelling the plates of an absorption column, Mc. Cabe Thiele method for the determination of the theoretical number of plates of a rectification column, graphical calculation of extraction using Gibbs triangle for Unit Operations, isothermal and non-isothermal batch reactor, isothermal plug flow reactor, real models for chemical reactors (axial mixing, Cholette-Cloutier) for Chemical Reactors.

All the animations presented in Table 1 are introduced in courses and they raise the level of understanding the teaching materials.

210 undergraduate students from the Faculty of Applied Chemistry and Materials Science, enrolled in the chemical engineering teaching domain, participated in the project. Several working groups assigned to a give course: Physical Chemistry, Chemical Engineering Fundamentals, Unit operations, Chemical Reactors were formed. A training program was organized for each group. The teaching materials available on the project platform were analyzed during this training program and each student realized a project using the new educational tools and specialized software: MathCad, Matlab, ASPEN-HYSYS, EXCEL, COMSOL.

Table 1.

Animations list

Animation number	Course	Animation
1	Physical Chemistry	Reversible and irreversible processes
2		Comparative presentation of the laws of ideal gas in 3D diagram
3		Multiple reactions. Calculation of the composition by using molar degrees of reactions advancement
4-5		Vapour – liquid equilibrium for a mixture with two components
6		Phases equilibrium for water; representation in 3D diagram
7		Gibbs triangle
8-9		Gibbs diagram and Carnot cycle (figure 1)
10		Azeotrope mixture
11	Chemical Engineering Fundamentals	Developing a technology
12		Absorption: establishment of the mass balance
13-14		Temperatures profiles and heat balance of a double pipe heat exchanger; influence of the flow rate on the heat balance (figure 2)
15-17		Modelling of non steady state heat balance for a mixed vessel; influence of the variation of the flow rate; influence of the lateral heat transfer
18		Mechanisms of heat transfer: conduction, convection, radiation.
19		Comparison between natural and forced convection
20	Unit Operations	Modelling of isothermal desorption of a gas from a liquid
21		Modelling of isothermal desorption of a gas from a liquid
22		Modelling the plates of an absorption column
23-25		Mc Cabe Thiele method for theoretical trays number calculation in a distillation column: influences of the operating parameters on the theoretical trays number (figure 3)
26		Operation of the distillation column at different thermal feed states
27		Graphical calculation of extraction using Gibbs triangle
28-31	Chemical Reactors	Isothermal plug flow reactor (PFD): concentration profile for a singular reaction of first order; influence of the input temperature and of the flow rate on the concentration profiles; concentration profile in the case of consecutive reactions
32		Isothermal batch reactor: consecutive reactions.
33		Thermal regime of the batch reactor (figure 4)
34		Ideal and real models for continuous stirred reactors: continuous stirring tank reactors (CSTR) and Cholette-Cloutier
35		Reactor with axial mixing

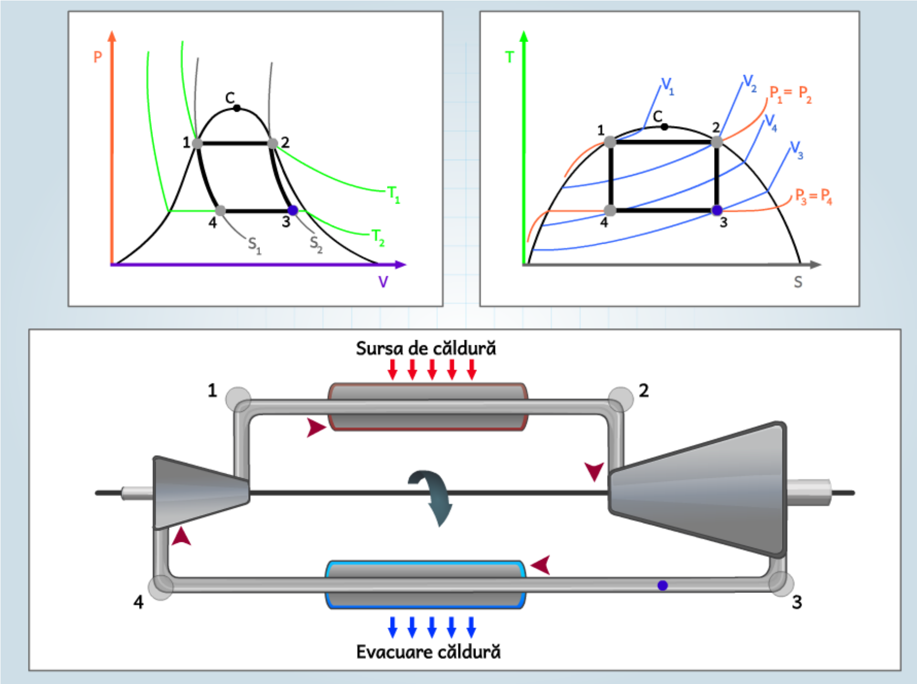

Fig. 1. Gibbs diagram and Carnot cycle, Physical Chemistry course

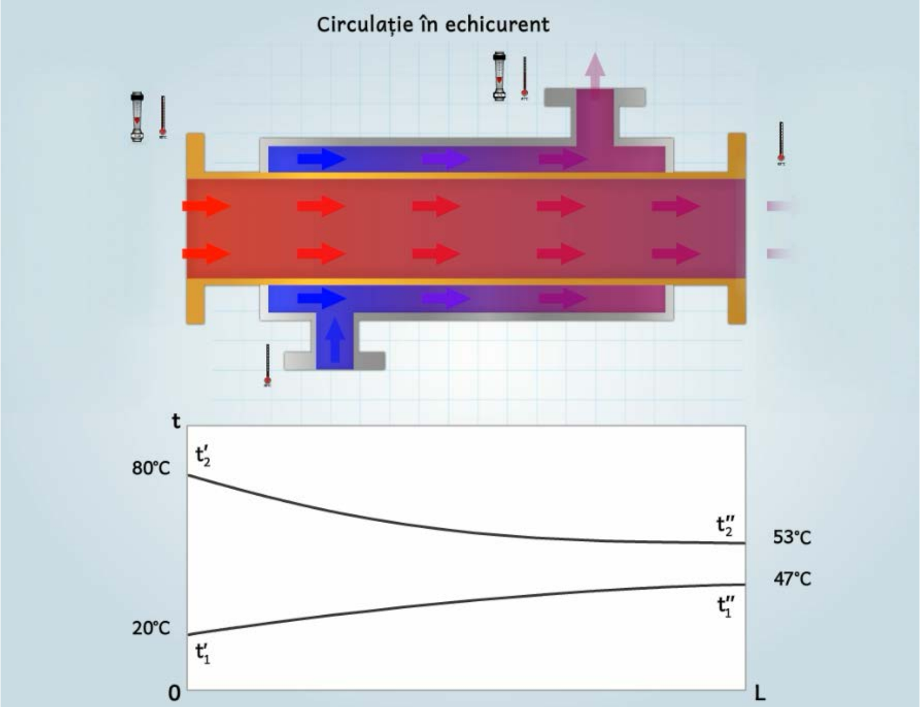

Fig. 2. Exemplification of heat balance calculation for tube in tube heat exchanger, Chemical Engineering Fundamentals course

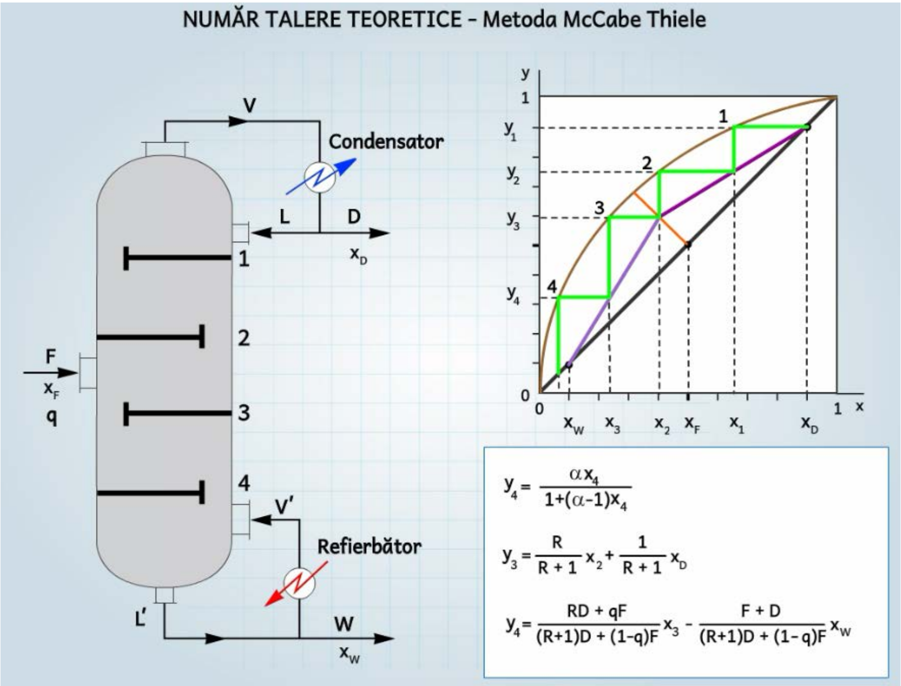

Fig. 3. Mc. Cabe Thiele method for theoretical trays number calculation in a distillation column, Unit Operation course

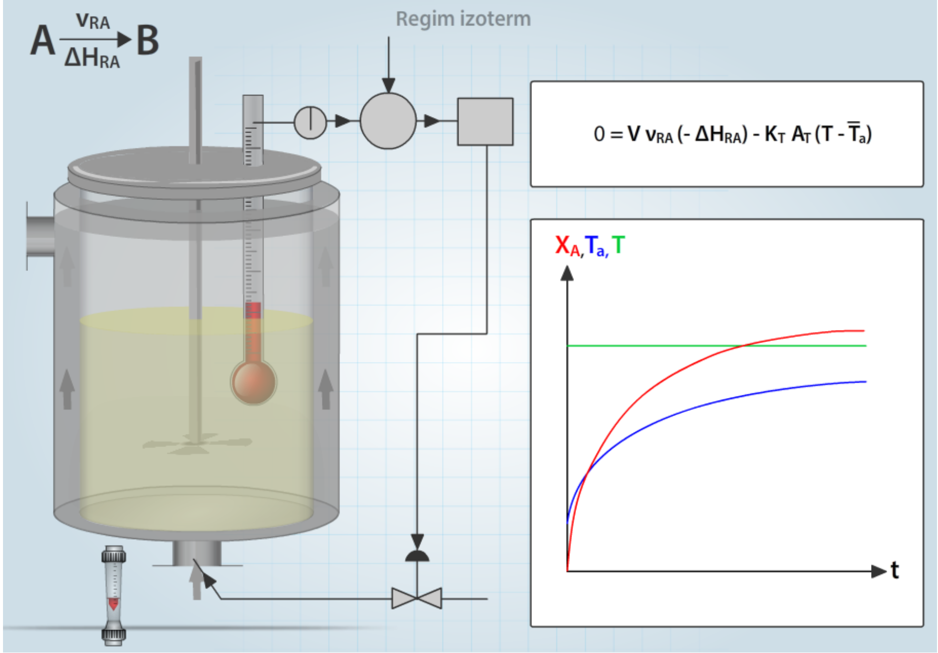

Fig. 4 Thermal regime of the batch reactor, Chemical Reactors course

3. Students opinions about the new teaching methods as revealed during formation program

All students participated at a survey to get a feed-back concerning the quality of the teaching materials created in the project, their contribution to a better understanding of the courses content and the advantages of using specialized software in solving chemical engineering problems.

A first general question aimed to identify the most important new features of the curriculum proposed in the project. The answers revealed that the most important new aspect are the use of software tools in the formation of a future chemical engineer, the increased importance of team working, and the application of theoretical knowledge in practical application –projects.

The influences of the new teaching methods implemented in the project were considered to considerably enhance the teaching efficiency in the chemical engineering field (Figure 5).

The greatest part of the students considered that a longer duration of the training courses and more multimedia animations would have helped more in the understanding of the phenomena of the processes. At the question: What have you expected to learn by participating to this project?” the students in the second year (Physical Chemistry and Chemical Engineering Fundamentals) mentioned the development of technical approach methods, learning to use computation software for engineering calculations such as MathCad and Matlab, a better understanding of various phenomena by means of multimedia tools, applying the theoretical knowledge in project type application.

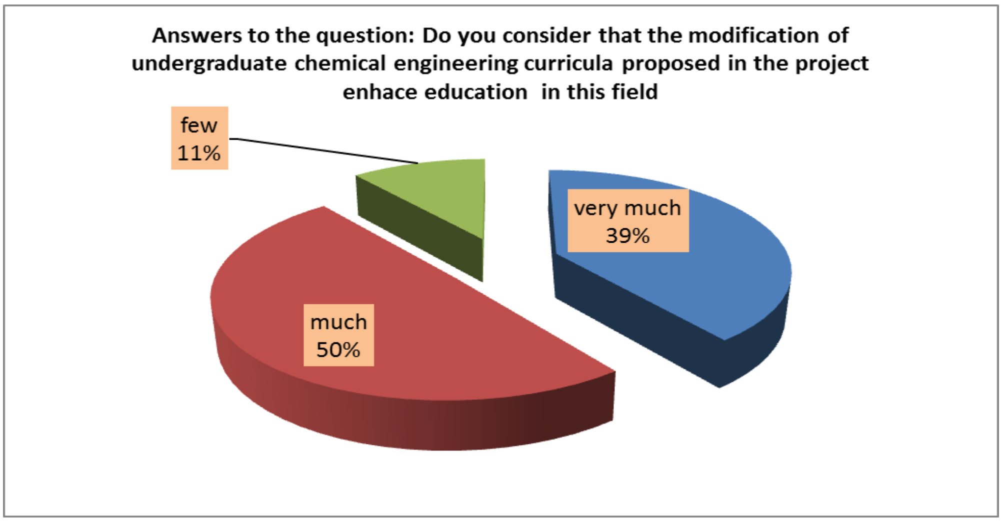

Fig. 5. The influence of new teaching methodes on enhancing students education

The students in the third and fourth year (Unit Operations and Chemical Reactors courses) also mentioned a better understanding of complex processes using multimedia tools and to acquire an increased ability in using specialized software such as Process Simulators and COMSOL.

The quality of training courses and working conditions were highly appreciated by a great majority of the students (Figure 6).

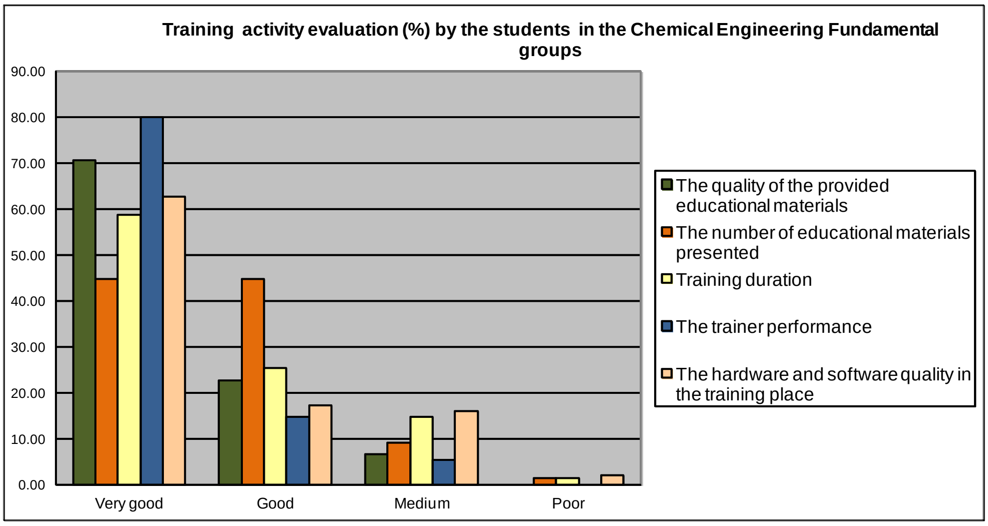

Fig. 6. Evaluation of training activity

The students also considered that the modifications proposed for the chemical engineering curricula and the multimedia materials will encrease the favorable image of the Faculty of Applied Chemistry and Materials Science and University Politehnica of Bucharest. (Figure 7).

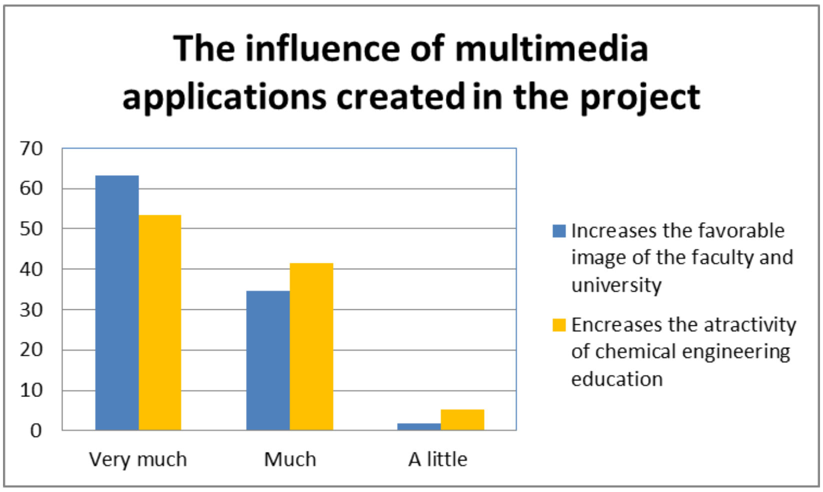

Fig. 7. The evaluation of multmedia application created in the project.

4. Conclusions

Video curses and multimedia applications were developed to enhance the efficiency of chemical engineering education in the faculty of Applied Chemistry and Materials Science from University POLITEHNICA of Bucharest. A survey addressed to the group of students involved in the project proved that learning by using multimedia applications brings important advantages in the understanding the main phenomena implied in chemical engineering processes.

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